Some co-ordination complexes of beryllium organoaluminium-silyl and -germyl complexes

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SOME CO-ORDINATION COMPLEXES OF BERYLLIUM

ORGANOALUMINIUM-SILYL AND -GERMYL COMPLEXES

by

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SUMMARY

This thesis can conveniently be divided into three parts.

Part 1

This part is concerned with attempts to synthesise and isolate complexes containing either aluminium-silicon or -germanium bonds. In no case has a stable complex been isolated. Some experiments, e.g. between Me_3Al and Me_3GeH, produced, rather surprisingly, no reaction while other approaches give products which can be accounted for if reactive aluminium-silicon or -germanium complexes are produced as reactive intermediates. In a few cases evidence (not entirely convincing) has been obtained for impure complexes e.g. ($Me_3SiAlMe_2$ T.H.F.) and $(Me_3Ge)_3Al$.

Part 2

This part of the thesis is concerned with some co-ordination complexes of organoberyllium compounds. No reaction was detected between tetramethyl-di-arsine and dimethylberyllium.

Dimethylberyllium reacts step-wise with tertbutylamine at ambient temperature to form the methyltertbutylaminoberyllium trimer and then the bis-tertbutylaminoberyllium dimer.

Dimethyl- and diethylberyllium etherates react with pyridine-2-aldehydephenylhydrazone with elimination of alkane to give the interesting coloured aminoberyllium compounds:

$$(MeBeC_{11}H_{11}N_3)_n \text{ and } EtBeC_{11}H_{11}N_3$$

Part 3

This part of the thesis is concerned with an investigation of the vapour phase association and fragmentation of the group III metal alkyls, Me_3M (M = B, Ga, In and Tl), and trivinylgallium, under electron impact.

Only in the case of trimethylgallium is there any evidence of low abundant (<0.1%) associated species although certain low abundant fragment ions in the mass spectrum of trivinylgallium could possibly be derived from higher oligomers. Variation of the abundances of the ions of all the alkyls with increasing source temperature and decreasing eV is discussed. The appearance potentials of the major ions in trimethylgallium were obtained, and the gallium-carbon mean bond strength is estimated.

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NOTE

The work described in this thesis was carried out in the University of Durham between September 1967 and August 1969 and in the Queen's University of Belfast between September 1969 and August 1970. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

PUBLICATIONS

Part of the work described in this Thesis has been included in the following publication:

"Alkylpolygermanes" J. Chem. Soc.(A), 1970, 426
(with F. Glockling and J.R.C. Light)

The author also gave a lecture "Catenated organogermanes" at the Joint Annual Meeting of the Chemical Society and the Royal Institute of Chemistry, Edinburgh April, 1970.
(with F. Glockling and J.R.C. Light)

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CHAPTER 1

ORGANOGERMYL AND-SILYL COMPLEXES OF ALUMINIUM

1.1 INTRODUCTION

In the alkylation of germanium halides by organoaluminium compounds, appreciable yields of catenated organogermanes are obtained[1,2,3]. The mechanism of formation of these oligomers is readily explained if reactive organoaluminium-germanium complexes are formed which react further to produce catenation. The purpose of this research was to attempt to isolate organoaluminium-germanium complexes and their silicon analogues, in order to substantiate this mechanism.

It is proposed in this section to discuss generally the synthesis and properties of alkyl-polysilanes and -germanes, to discuss in more detail reactions where aluminium - group IVb complexes are thought to play an important part and then to briefly review the synthesis and properties of known organo-silyl and -germyl main group organometallic complexes.

1.1.1 Synthesis and Properties of Alkyl-Polysilanes

Six years after the preparation of the first organosilicon compound, Et_4Si, Friedel and Ladenberg reported the synthesis of hexaethyldisilane in 1869[4]. This was the first catenated derivative of this class of compound and involved the reaction of hexaiododisilane with diethylzinc(I).

$$I_3Si\text{-}SiI_3 + 3Et_2Zn \longrightarrow Et_3\text{-}Si\text{-}SiEt_3 + 3\ ZnI_2 \qquad (I)$$

Since then, until recently, only a limited number of alkyl derivatives of polysilanes had been made and these were mostly hexaalkyldisilanes. During the last fifteen years however, advances have been made and the chemistry of alkylpolysilanes has been the subject of several reviews[5,6,7], the most recent being by K.M. Mackay and R. Watt[7].

1.1.2 Synthesis

Essentially, the polysilanes are synthesised by the same methods used

for the lowest member of the class, the disilanes, and the following syntheses describe the formation of disilanes followed by the applicability of each method for higher polysilanes.

(a) From Si_2X_6 and Organometallic Reagents (X = halogen)

This was the first method[4], and since then, many other organometallic reagents including Grignards[8] and alkyl-lithium[9] compounds have been used for the preparation of disilanes. Steric factors can become important in these reactions. This method is not very applicable to the formation of alkyl polysilanes as alkylation of the halopolysilanes usually proceeds with some Si-Si bond cleavage.

(b) Wurtz Type Reactions

This is the most convenient and generally applicable method and involves condensation of methylhalosilanes (usually the chlorosilanes) by treatment with Na, K, or Li. This method was first employed by Schlenk[10] in attempting to make the triphenylsilyl radical (2).

$$2Ph_3SiCl + 2Na \longrightarrow Ph_6Si_2 + 2NaCl \qquad (2)$$

The synthesis of disilanes by this method has been extensively investigated and it has been found that the coupling of chlorotrimethylsilane using Na/K alloy proceeds in the absence (75% yield[11]) as well as in the presence of an inert solvent such as xylene (69% yield[12]) and tetrahydrofuran[11]. The Wurtz method is used to synthesisethe homologous series of linear polysilanes of the general formula $Me(SiMe_2)_nMe$[11,12,13] (3).

$$Me_3SiCl + Me_5Si_2Cl \xrightarrow{Na/K} Me_8Si_3 \qquad (3)$$

Slight experimental complications arise when higher homologues than the tetrasilanes are formed, in that separations of the consecutive members

e.g. $Me_{10}Si_4$ and $Me_{12}Si_5$, is difficult to achieve. To this end it is desirable to choose the two chlorosilanes employed such that the products differ by at least two silicon atoms and separation is then easily accomplished (4).

$$2Me_3SiCl + x\ Cl\left[SiMe_2\right]_{3,5,7}Cl \xrightarrow{Na/K} Me(SiMe_2)_nMe \qquad (4)$$

$$n = 5,\ 8,\ 11.$$

Reaction of the appropriate diorganodihalosilane with metals gives cyclosilane derivatives[14], (5),

$$Me_2SiCl_2 + Na/K \xrightarrow{T.H.F.} \left[Me_2Si\right]_6 \qquad (5)$$

and it has been suggested[7] that the heavier metals of Group IVb could form more stable small cyclic compounds than their carbon analogues.

(c) Silyl-metallic Reagents

These are typified by the reaction (6)

$$4Me_3SiLi + SiCl_4 \longrightarrow (Me_3Si)_4Si + 4LiCl \qquad (6)$$

and are generally useful if chain branching is required and/or if unsymmetrical organosilanes are wanted. The uses of silyl-metallic reagents has been reviewed[14].

(d) Miscellaneous

These methods include the decomposition of tetramethylsilane by electrical discharge and the direct synthesis of methylchlorosilanes (from Si and MeCl) which gives a variety of compounds containing Si-Si bonds. The disadvantages of these methods are in their non-specificity but the latter "direct synthesis" has industrial advantages.

1.1.3 Physical Properties

Permethylated linear polysilanes are stable, colourless liquids or white crystalline substances. The cyclic and branched polysilanes are white crystalline solids with relatively high melting points. They are stable to heat and usually can be heated to their melting point without decomposition. Hexamethyldisilane is partly decomposed at 600° into trimethylsilane and trimethyl(dimethylsilylmethyl)silane together with the unchanged disilane[15].

$$Me_3SiSiMe_3 \xrightarrow{600^\circ} Me_3SiCH_2SiMe_2H + Me_3SiH \qquad (7)$$

1.1.4 Spectral Studies

(a) Infra-red

The infra-red spectra of R_3Si compounds have been the subject of a recent review[16]. Some alkyl polysilanes including $Me_{10}Si_4$ and $Me_{12}Si_5$ have also been studied[17]. Generally ν(Si-Si) is at 358-442 cm^{-1}, νsym(Si-C) is at 620-670 cm^{-1} and $\nu(CH_3)$ is at 2890-2950 cm^{-1}. The Raman spectra have also been studied[17].

(b) Ultra violet

One of the more interesting properties of alkyl-polysilanes is that they absorb in the ultra-violet[5,18]. Generally intense absorption maxima are seen and λmax and extinction coefficients increase fairly regularly with increasing chain length. Cyclic and branched polysilanes absorb at lower wavelengths than the corresponding open chain analogues[5]. These spectral properties are probably due to the Si-Si bond acting as a chromophore with some "double-bond" character due d^{π}-d^{π} interaction of vacant d-orbitals on the silicon atoms.

(c) N.m.r.

The p.m.r. spectra of polyalkysilanes have recently been reviewed[6,19]. For linear permethyl polysilanes the chemical shift of the methyl protons

generally appears at a lower field as the distance of the methyl group from the end of the chain increases. Octamethyltrisilane represents an exception in which the chemical shift for methyl proton on the central Si atom is at a slightly higher field than for the terminal methyl groups. This fact can be understood by consideration that in longer silanes, on conformational grounds there is considerable interaction between internal methyl groups and methyl groups two silicon atoms distant in the chain, in Me_8Si_3 there is no such interaction.

(d) Mass Spectra

This is discussed more fully in section 3.1.11 of this thesis.

1.1.5 Chemical Studies

The silicon-silicon bond strength in hexamethyldisilane and higher homologues is fairly high being about 80 kcal. $mole^{-1}$, compared to the mean silicon-carbon bond energy of 70 kcal. $mole^{-1}$ [20].

Thus reactions of alkyl-polysilanes, involving cleavage of the Si-Si bond need comparatively high activation energies.

Alkyl-polysilanes with silicon functional groups react in a similar way to the corresponding monosilanes and keep the silicon chain intact[21] (8).

$$ClCH_2[SiMe_2]_2CH_2Cl + NaI \xrightarrow{\text{acetone}} I\text{-}CH_2[SiMe_2]CH_2Cl + NaCl \qquad (8)$$

Cleavage of the Si-Si bond in alkyl-polysilanes can be achieved using a variety of electrophilic reagents including halogens[5,20] hydrogen halides, inorganic halides and alkyl halides[5] giving generally the trialkylsilyl halide. With the higher homologues, careful reaction control is needed to give the required products. Bromination has also been used to deduce structures and the number of silicon atoms present in linear permethylated polysilanes.

Nucleophilic cleavage of the Si-Si bond can generally be achieved with a variety of media including aqueous piperidine and alcoholic alkali[22,23]. By far the most interesting nucleophilic cleavage is that by metals and this has been extensively studied[5,14]. Silylmetallic reagents are formed and these are of general use in synthetic organometallic chemistry. The optimum cleavage of hexa-aryldisilanes is with lithium shot in T.H.F. (7).

$$Ph_6Si_2 + 2Li \longrightarrow Ph_3Si^-Li^+ \qquad (7)$$

Hexaalkyl disilanes do not undergo such cleavage although higher homologues do, using Na/K alloy. The reason is probably because the negative charge can be spread over several silicon atoms thus stabilising the anion in the higher homologues. Generally the longer the chain the easier the cleavage is to effect.

The chemistry of the alkyl-polysilanes, in general, is only at an exploratory stage and many interesting questions are awaiting study.

1.1.6 Synthesis and Properties of Alkyl Polygermanes

The synthesis and properties of catenated organogermanes have recently been reviewed[1,2,3,5,6,7]. The first catenated germane, Ph_6Ge_2, was prepared in 1925 by G.T. Morgan and H.D. Drew from the Wurtz reaction on Ph_3GeBr[25]. They may conveniently be divided into four sub-groups: (a) digermanes, (b) cyclic organopolygermanes, (c) linear and branched chain species and (d) ill-defined high polymers.

(a) Digermanes

Wurtz-type syntheses form the basis of the most general method for the preparation of hexaorganodigermanes.

$$2R_3GeX + 2M \longrightarrow R_6Ge_2 + 2MX$$

Yields are about 50%, and on closer investigation of the residue higher germanes are found[1,2]. For example, Me_3GeBr/K yields

trimethylgermylpentamethyldigermanylmethane, $Me_3Ge(Me)_2Ge-CH_2GeMe_3$ and tetrakis trimethylgermylgermane, $(Me_3Ge)_4Ge$[1]. These may be considered formed by the mechanisms (8) and (9).

$$Me_3GeBr \xrightarrow{2K} Me_6Ge_2 \xrightarrow{2K} Me_3Ge\text{-}Ge(Me_2)CH_2K + KH$$

$$\downarrow Me_3GeBr \qquad (8)$$

$$Me_3Ge(GeMe_2)CH_2GeMe_3 + KBr$$

$$Me_6Ge_2 \xrightarrow{2K} Me_3Ge\text{-}GeMe_2K \xrightarrow{Me_3GeBr} Me_3GeGeMe_2\text{-}GeMe_3$$

$$\downarrow \begin{matrix}1.2\ K \\ 2.2\ Me_3GeBr\end{matrix} \qquad (9)$$

$$(Me_3Ge)_4Ge$$

Digermanes are also formed by coupling Grignard reagents. The mechanism of this probably involves "germyl Grignard reagents", R_3GeMgX species[26,27]. The evidence for their existence is reasonably well established, since carefully filtered solutions of, for example, PhMgBr and $GeCl_4$ give high yields of Ph_4Ge whereas with excess magnesium, 70% of Ph_6Ge_2 is formed[27]. (10).

$$Ph_3GeBr + Mg \longrightarrow Ph_3GeMgBr \xrightarrow{Ph_3GeBr} Ph_6Ge_2 + MgBr_2 \qquad (10)$$

Higher germanes may also be formed, as from vinylmagnesium bromide and $GeCl_4$, where octavinyltrigermane as well as hexavinyldigermane, has been identified[28].

Generally the yield of catenated organogermanes from $GeCl_4$ and Grignard reagents depends on the steric properties of the original organic halide and the solvent used as well as the presence of free magnesium.

Other organometallic reagents such as alkyl-lithium and organo-

aluminium compounds produce on reaction with $GeCl_4$ digermanes and higher homologues. In the alkylation of $GeCl_4$ by AlR_3 compounds the yield of digermane increases in the order, Me<Et<Bu^i.

Unsymmetrical digermanes are produced by condensation reactions on a preformed triorganogermyl-alkali metal derivative (II).

$$Ph_3GeNa + Et_3GeBr \xrightarrow{NH_3} Ph_3GeGeEt_3 \qquad (II)$$

The yields are low owing to halogen-metal exchange and coupling to give the symmetrical digermanes[29,30].

(b) Cyclic Organopolygermanes

These are made by applying the Wurtz reaction to di-organodihalogermanes. This reaction produces both cyclic and high molecular-weight linear or branched-chain polymers. Six-membered rings are the largest so far isolated[31,32] (12).

$$Ph_2GeCl_2 \xrightarrow{Na} (Ph_2Ge)_4 + (Ph_2Ge)_5 + (Ph_2Ge)_6 \qquad (12)$$

Reduction of dimethyldichlorogermane by lithium leads to a cyclic hexamer together with polymeric products[33].

$$Me_2GeCl_2 \xrightarrow{Li/T.H.F.} (Me_2Ge)_6 + \text{higher polymers}$$

Linear and branched chain polymers

These are formed in isolable yields as by-products in the alkylation of germanium halides by Grignard reagents, alkyl-lithium compounds, organoaluminium compounds and the Wurtz reaction.

One interesting observation is that in the alkylation of the germanium halides by, for example Me_3Al, lengthening of the alkyl chain takes place[1,2]. The mechanism of formation and deduction of structure of the alkyl polygermanes are discussed in sections 1.1.8 and 1.1.10 of this thesis.

In general however specific catenated organogermanes can be synthesised by generating the R_3Ge^- anion and reacting with a germanium halide (13).

$$Me_3Ge^-Li^+ + GeCl_4 \longrightarrow (Me_3Ge)_4Ge + 4LiCl \qquad (13)$$

(d) Ill-defined High Polymers

Various reactions have been reported as yielding polymeric organogermanes which necessarily require extensive metal-metal bonding. For example, Ph_2GeCl_2 reacts with sodium in boiling xylene to give as well as the tetramer $(Ph_2Ge)_4$ in 10-20% yield, a yellow residue which has a mean molecular weight of 900. Degradative bromination indicates the presence of Ph_3Ge^-, Ph_2Ge^- and $PhGe^-$ units giving a composition intermediate between Ph_2Ge and PhGe.

Similar residues are obtained by reaction of PhLi and Ph_3Al with GeI_2 [34]. This can be interpreted by assuming that phenylation of GeI_2 is in competition with halogen-metal exchange so that germanium-metal bonded species are intermediates in the polymerisation process.

1.1.7 Physical Properties

Alkyl-polygermanes are colourless, viscous high boiling liquids. They have a characteristic sweet smell and are stable to hydrolysis and air although the higher methylgermanes tend to oxidise after about 15 minutes exposure, forming cyclic oxides[1].

Little work has been done on the thermal stability of even the simpler hexa-alkyl digermanes although generally the methylpolygermanes survive g.l.c. at 230°.

Pyrolysis of $(Me_2Ge)_n$ at 400° results in degradation to the cyclic hexamer $(Me_2Ge)_6$[2].

1.1.8 Spectroscopic Properties

(a) Infra-red and Raman

Infra-red spectra of the organogermanes Ge_nR_{2n+2} are strikingly similar to those of the corresponding digermanes. Typical values are: $(Me_3Ge)_4Ge$, ν(CH) 2967 and 2899 cm^{-1}; $\delta sym(CH_3)$ 1236 cm^{-1}; $\rho(CH_3)$ 826 cm^{-1}; ν(Ge-C) 593 and 556 cm^{-1}. The intensity of the lower frequency Ge-C stretch increases with the number of germanium atoms and for penta- or higher germanes the two bonds are of equal intensity[1,2].

Deduction of the structure of higher polygermanes from Ge-Ge stretching modes in the far infra-red has not been as successful as Raman investigations of this region[35].

The Raman spectra of Me_6Ge_2 and higher alkyl polygermanes have been studied and ν(Ge-Ge) is placed at 250-300 cm^{-1}. [36,37]

(b) Ultra-violet

The catenated organogermanes absorb in the ultra-violet, probably due to some degree of germanium-germanium multiple bonding acting as a chromophore[38,39]. Digermanes absorb strongly in the near u.v. and with alkylgermanes, both Σ and λmax increase with the length of the alkyl groups.

(c) N.m.r.

The proton magnetic resonance spectra of methyl polygermanes have been the subject of a recent paper[37]. In these spectra, couplings in the 'H-H proton-proton systems 'H-C-Ge-C-H' and H-C-Ge-Ge-C-H' were not detected and so the spectra were relatively simple.

Generally the chemical shifts were in the order $Me_3Ge > Me_2Ge > MeGe$, as for methyl polysilanes and stannanes, and solvent effects were noted with CCl_4 and benzene.

an isomer of

The use of p.m.r. in structure determination is seen with $Me_{10}Ge_4$. This compound has methyl resonances of relative areas 9 : 1. The structure is hence $(Me_3Ge)_3GeMe$.

By the same token proton magnetic resonance when combined with mass spectroscopy can lead to complete structure determinations. For example, the compound $C_{11}H_{32}Ge_4$ is shown by mass spectrometry to be Me_9Ge_4Et since its fragmentation pattern includes several metastable peaks due to ethylene elimination. The position of the ethyl group cannot be deduced from the mass spectrum however, but the p.m.r. shows three MeGe resonances of relative areas 6:2:1, indicating that the ethyl group had replaced one of the trimethylgermyl methyl groups, (i.e. $(Me_3Ge)_2GeMeGeMe_2Et$).

High resolution p.m.r. spectra also differentiates between the isomers tetrakistrimethylgermylgermane $(Me_3Ge)_4Ge$ and 2-trimethylgermyl-nonaamethyltetra-n-germane $(Me_3Ge)_2GeMeGeMe_2GeMe_3$.

(d) Mass Spectra

The mass spectra of organogermanes have been the subject of several papers[1,2,40] and are discussed more fully in section3.1.11 of this thesis. However, generally the molecular ion is always present and fragmentation/rearrangement processes involve loss of an alkyl radical (or alkene) and $R_2Ge^{+\cdot}$ with corresponding metastable peaks.

1.1.9 Chemical Studies

The strength of the Ge-C bond is approximately 71 kcal. $mole^{-1}$ while the Ge-Ge bond strength is around 60 kcal. $mole^{-1}$ [2]. Thus cleavage reactions which are relatively easy to accomplish, have been the most studied reaction of alkyl germanes. Hot oxidising acids, for example, degrade alkyl-polygermanes to give germanium dioxide. Halogens, inorganic halides and alkyl halides all react under fairly mild conditions to give

various substituted halogermanes.[2]

Aluminium trichloride reacts with Et_6Ge_2 at 200° to give further decomposition products[41] (14).

$$Et_6Ge_2 \xrightarrow{AlCl_3} Et_4Ge + (EtGe)_n + \text{hydrocarbons} \qquad (14)$$

Cleavage of the digermanes by alkali metals is profoundly influenced by the solvent used and as in the case of silyl-metallics, the triarylgermyl metal compounds are more stable than the trialkyl analogues. Triethylgermylpotassium was first obtained by using Et_6Ge_2 and K in ethylamine[42] (15).

$$Et_6Ge_2 + 2K \xrightarrow{EtNH_2} 2Et_3GeK \qquad (15)$$

Similarly triethylgermyllithium has been made in liquid ammonia but it readily solvolysed to triethylgermane and lithamide (16).

$$Et_6Ge_2 + 2Li \xrightarrow{NH_3} 2Et_3GeLi \xrightarrow{NH_3} Et_3GeH + LiNH_2 \qquad (16)$$

Germylmetallics have been used in the synthesis of unsymmetrical digermanes, higher catenated organogermanes and other organometallic metal-metal bonded complexes. A more recent solvent used is hexamethylphosphortriamide, $(Me_2N)_3PO$. This solvent readily dissolves alkali metals forming change-transfer complexes and reacts with R_3GeBr to form stable solutionsof reddish-brown R_3GeM compounds[43].

However its use as a solvent in preparative organometallic chemistry is limited because of its intractability and difficulty in separation from compounds with high boiling points.

1.1.10 Suspected Organo-silyl- and -Germyl-Aluminium Complexes as Intermediates

(a) Suspected organo-silyl-aluminium intermediates

There are several reactions involving organosilicon compounds which

are known to be "catalysed" by the presence of aluminium chloride in large amounts[44]. (17)

$$ClSiMe_2SiMe_2CH_2Cl \xrightarrow{AlCl_3} ClSiMe_2CH_2SiMe_2Cl \qquad (17)$$

While not implying a definite silicon-aluminium intermediate in the above type of reactions, which probably involve halogen exchange type processes, there are reactions in which the presence of an aluminium-silicon intermediate is required. H.A. Gilman and R.A. Thomas investigated[45] the reactions between $LiAlH_4$ and a number of phenylated disilanes. They found that the rate of reaction (18)

$$R_3Si\text{-}SiR_3 + H^- \longrightarrow R_3SiH + R_3Si^- \xrightarrow{H^+} 2R_3SiH \qquad (18)$$

decreased as the phenyl groups were replaced by alkyl groups and that with Et_6Ge_2 no triethylsilane was observed.

They also added Me_3SiCl to the reaction mixture, from hexaphenyldigermane and $LiAlH_4$ prior to hydrolysis, and obtained no 1,1,1-trimethyl-2,2,2-triphenyldisilane which would probably have been formed if a Ph_3Si^- anion was present. However on hydrolysis with D_3O^+, triphenylsilane-d, Ph_3SiD, was obtained. This must imply an organo-silicon-aluminium intermediate as in the following mechanism (19).

$$Ph_6Si_2 + LiAlH_4 \longrightarrow Ph_3SiH + Li^+[Ph_3Si\text{-}AlH_3]^- \xrightarrow{3Me_3SiCl} \qquad (19)$$

$$Ph_3SiD \xleftarrow{D_3O^+} Ph_3SiAlCl_2 \xrightarrow{Me_3SiCl} \text{no reaction}$$

Aluminium metal itself does not cleave Ph_6Si_2 or react with Ph_3SiCl even in refluxing tetrahydrofuran, to form aluminium-silicon compounds.

Another reaction in which aluminium-silicon intermediates are postulated to play an important part is between bis(trimethylsilyl)mercury and aluminium. Wiberg et al.[46] expecting to make $Al(SiMe_3)_3$, instead

found that the reaction had gone in an entirely different way (20).

$$Al + (Me_3Si)_2Hg \xrightarrow[3\ days]{60^o} AlMe_3 + Me_6Si_2 + Me_8Si_3 + Me_{10}Si_4 + Hg \qquad (20)$$

The reaction is postulated, reasonably, to have the following mechanism (21) with dimethylsilene being formed.

$$\begin{aligned} Al + (Me_3Si)_2Hg &\longrightarrow Al(SiMe_3)_3 + Hg \\ Al(SiMe_3)_3 &\longrightarrow AlMe_3 + 3Me_2Si: \end{aligned} \qquad (21)$$

The dimethylsilene then reacts with $(Me_3Si)_2Hg$ to form $Me_3Si.HgSi_2Me_5$ and $Me_5Si_2Hg.Si_2Me_5$ which decompose to give the Me_8Si_3 and $Me_{10}Si_4$ compounds. This reaction is similar to the Ziegler polymerisation of ethylene.

The decomposition of the tris(trimethylsilyl)aluminium is analogous to the decomposition of tri-isobutylaluminium at 200°.[47] (22)

$$Al(C_4H_9)_3 \xrightarrow{200^o} (AlMe_3) + 3C_3H_6 \qquad (22)$$

Reaction of bis-trimethylsilylmercury with dimethylaluminium hydride at room temperature gave trimethylsilane, trimethylaluminium and $Me_{10}Si_4$ and Me_8Si_3. The mechanism of this reaction is postulated in a similar way (23).

$$\begin{aligned} (Me_3Si)_2Hg + Me_2AlH &\longrightarrow Me_3SiH + Me_2Al\text{-}SiMe_3 + Hg \\ Me_2AlSiMe_3 &\longrightarrow AlMe_3 + :SiMe_2 . (Me_3Si)_2Hg + Me_2Si: \longrightarrow Me_8Si_3 + Me_{10}Si_4 \end{aligned} \qquad (23)$$

(b) Suspected Organogermyl-aluminium Complexes as Intermediates

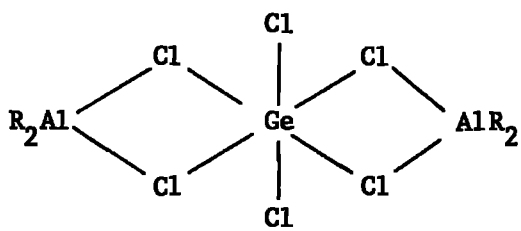
Unlike the analogous silicon complexes, there was little evidence for the presence of organogermanium-aluminium complexes other than the catenated by-products formed in the alkylation of germanium halides by organoaluminium compounds[48].

using aluminium alkyls

Although the alkylation of germanium halides has similarities to the Grignard reaction with germanium tetrachloride there are differences, including for example, complications due to partial alkylation which are absent when using organoaluminium compounds. However, in all cases, $GeCl_4$ is isolated even when a large excess of R_3Al is used[1,3]. These observations are consistent with the rate of mono-alkylation being the slowest step in contrast to the Grignard reaction where substitution of the fourth halogen is usually the slowest. This leads to an accumulation of partially chlorinated aluminium compounds in the reaction mixture (24).

$$2GeCl_4 + (R_3Al)_2 \longrightarrow 2RGeCl_3 + (R_2AlCl)_2 \qquad (24)$$

It is quite possible that at this stage formation of a halogen-bridged complex between $(R_2AlCl)_2$ and $GeCl_4$ would occur (25).



(25)

Germanium tetrachloride is known to form octahedral complexes (such as $GeCl_6^{2-}$), but substitution of Cl by R greatly reduces the acceptor power of germanium[49]. Hence any transfer of R to the germanium would cause immediate disruption of the complex and the $RGeCl_3$ liberated would be rapidly alkylated.

Some Russian work has also indicated, by colour change and evolution of heat, the presence of an complex between Et_3Al and $GeCl_4$ on heating at 130° for 3-5 hours[50]. On hydrolysis, Et_2GeCl_2 can be isolated in 76% yield implying an ($Et_2GeCl_2AlEtCl_2$) type complex.

The reactions between R_3Al and $GeCl_4$ and GeI_2 are summarised in Fig. 1.

Fig. 1

Summary of Alkylation Products From R_3Al With Germanium Halides

(J.R.C. Light, Ph.D. Thesis, Durham 1968)

(i) $Me_3Al + GeCl_4 \longrightarrow$ Me_4Ge (60-80%) + Me_6Ge_2 + $Me_{n+2}Ge_n$ (n = 4,5,6), Me_7Ge_3Et, $Me_6Ge_3Et_2$, Me_9Ge_4Et.

(ii) $GeCl_4 + Et_3Al \longrightarrow$ Et_4Ge, $Et_6Ge_2Et_3GeBu^n$, $Et_3GeC_6H_{13}Et_5Ge_2Bu$, $Et_5Ge_2C_6H_{13}$, $C_{18}H_{42}Ge_2$, (possibly $Et_3Ge_2Bu_3$), Et_7Ge_3Bu, $Et_7Ge_3C_6H_{13}$.

(iii) $GeCl_4 + {}^iBu_3Al \longrightarrow$ ${}^iBu_4Ge$, ${}^iBu_6Ge_2$ + ${}^iBu_8Ge_3$.

(iv) $GeI_2 + Me_3Al \longrightarrow$ $Me_{10}Ge_4$, Me_9EtGe_4, Me_9PrGe_4, $Me_8Ge_4Et_2$, $Me_{12}Ge_5$, $Me_{11}EtGe_5$ + $Me_{n+2}Ge_n$ (n = 6,7,8, 9,10).

(v) $GeI_2 + Et_3Al \longrightarrow$ Et_6Ge_2, Et_8Ge_3, $Et_{10}Ge_4$.

(vi) $GeI_2 + {}^iBu_3Al \longrightarrow$ ${}^iBu_5Ge_2I$ + ${}^iBu_7Ge_3I$ + ${}^iBuGeI_3$ + GeI_4 + higher polymers.

The mechanism of formation of the polygermanes and the lengthening of the alkyl chains is rather obscure. There are three possible mechanisms for the formation of polygermanes from $GeCl_4/R_3Al$ mixtures[1,2,3]. The first involves a reactive Ge-Al intermediate analogous to the germyl Grignard reagent (26).

$$2GeCl_4 + 2R_3Al \longrightarrow R_3GeCl + (R_2AlCl)_2 \qquad (24)$$

$$R_3GeCl + (R_3Al)_2 \longrightarrow R_3Ge\text{-}\underset{\displaystyle R}{\overset{\displaystyle R}{Al}}\text{-}\underset{\displaystyle R}{\overset{\displaystyle R}{Al}}\text{-}AlR_2 + RCl$$

$$\downarrow \; R_3GeCl \qquad (26)$$

$$R_3Ge\text{-}GeR_3 + R_5Al_2Cl$$

Such complexes would have to be highly reactive since no R_3GeH is formed prior to hydrolysis[1]. The formation of organopolygermanes would require redistribution followed by more coupling etc. (27)

$$R_3Ge\text{-}GeR_3 + GeCl_4 \longrightarrow R_3Ge\text{-}GeR_2Cl + RGeCl_3$$

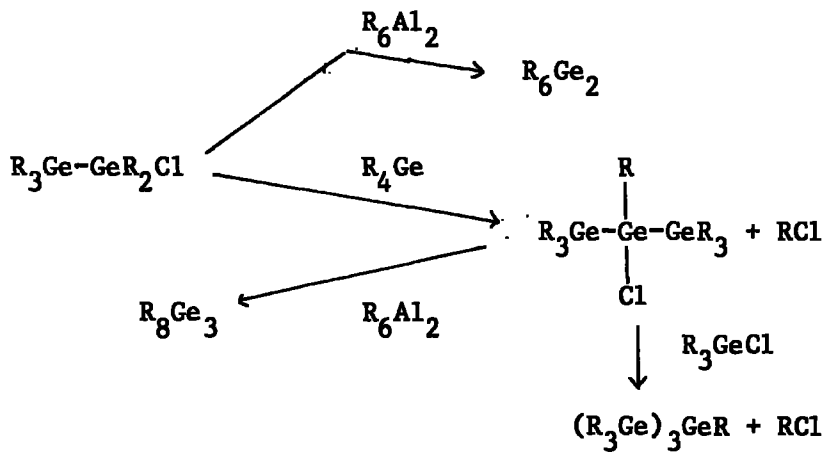
$$\downarrow \; R_6Al_2$$

$$R_3Ge\text{-}GeR_2\text{-}\underset{\displaystyle R}{\overset{\displaystyle R}{Al}}\text{-}\underset{\displaystyle R}{\overset{\displaystyle R}{Al}}\text{-}AlR_2$$

$$R_8Ge_3 + R_5Al_2Cl \xleftarrow{R_3GeCl}$$

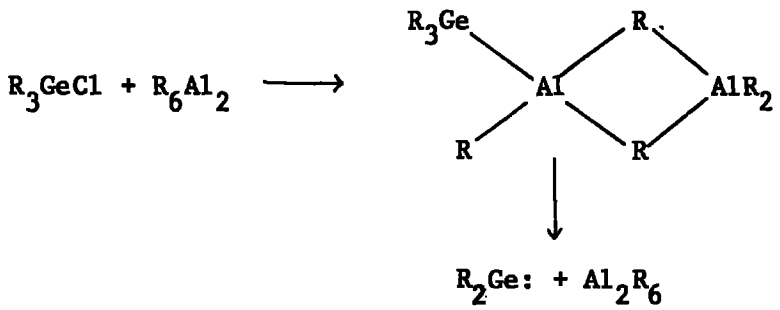
(27)

A second mechanism involves a Ge^{IV}-Ge^{II} reduction with the Al compounds acting solely as alkylating agents (28).

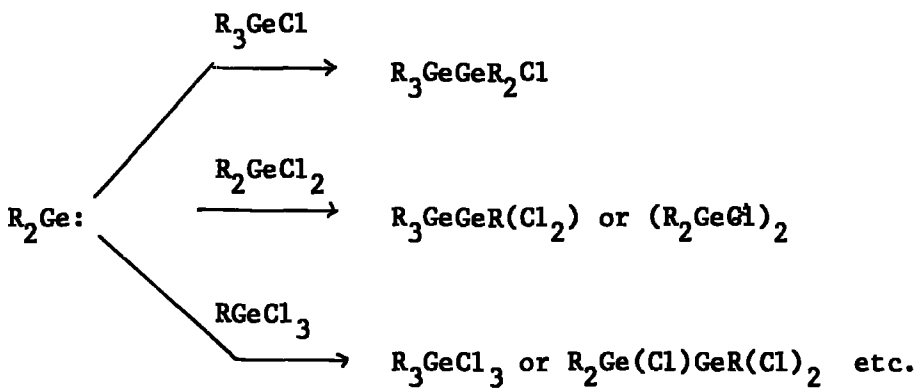


(28)

A third possible mechanism has features of the last two mechanisms, and the formation of a reactive dialkylgermane [illegible] (29).



(29)



The "R_2Ge:" moiety is possibly similar to that postulated to be generated from Al and $(Me_3Si)_2Hg$.[46]

Differences between the above mechanisms are marginal and increases of di- and polygermanes formed in the series Me<Et<^{i}Bu may be due to

steric factors. The formation of $Ge-CH_2-Ge$ groups can also be explained if chlorination by $AlCl_3$ and further condensation reactions are invoked. Under far more drastic conditions than those used, Me_3GeCH_2Cl is known to rearrange to $Me_2GeEtCl$ when heated in the presence of $AlCl_3$.[51]

The alkylation of germanium diodide by R_3Al compounds has several differences from the alkylation of germanium tetrachloride. The presence of iodogermanes, $^{i}Bu_5Ge_2I$, reflect the steric effect of the iso-butyl groups.

The mechanism of formation of the polygermanes remains a little obscure. Efforts were made to ensure that Ge(II) iodide was clear of Ge(IV) impurities and so at some stage an oxidation occurs. Neither germanium or aluminium metal separates and so the presence of a low valency aluminium or germanium complex is assumed. Aluminium (I) intermediates have been postulated in other reactions.[52]

Terminal Me_3Ge groups may arise via highly reactive intermediates such as $Me_3Ge-AlMe_2$ or $Me_3Ge-AlI_2$ formed by successive methylation of GeI_2. These are not present at the end of the reaction as hydrolysis does not produce any Ge-H containing products.

Formation of Ge-Ge bonds could also occur in insertion reactions such as (30) where the product would probably be halogen bridged.

$$Me_3Ge-AlI_2 + GeI_2 \longrightarrow Me_3Ge-GeI_2AlI_2 \qquad (30)$$

Chain branching could also arise in a variety of ways as in (31).

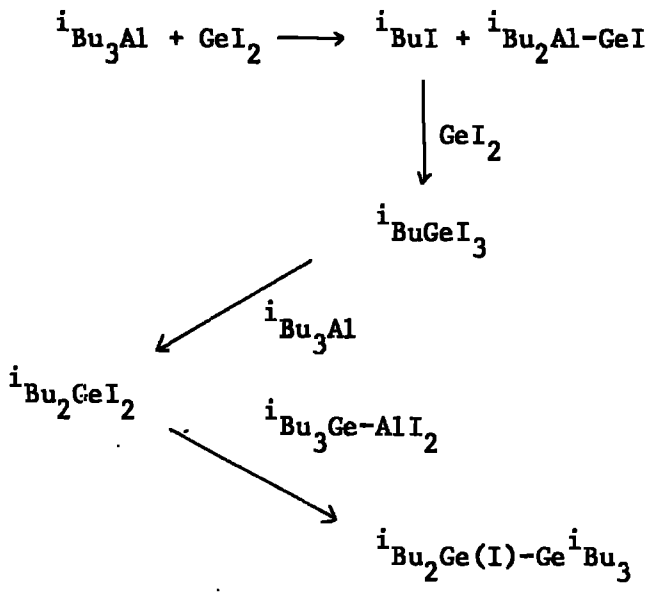
$$Me_3Ge-GeI_2AlI_2 + Me_3GeAlI_2 \longrightarrow (Me_3Ge)_2GeIalI_2 + AlI_3 \qquad (31)$$

and Ge containing end products might be produced by (32).

$$(Me_3Ge)_2Ge-Me-AlI_2 + Me_3GeAlI_2 \longrightarrow (Me_3Ge)_3GeMe + Al_2I_4 \qquad (32)$$

In the reaction of $^{i}Bu_3Al$ with GeI_2 more lower germanes are formed,

probably due to steric influences. The suggested mechanisms for the reactions of $^{i}Bu_3Al$ and GeI_2 are shown (33).



(33)

The formation of products resulting from the growth of alkyl chains pose similar problems. These probably arise from $GeCH_2\text{-}Al$ or $GeCH_2I$ intermediates. However deuterolysis gave no $GeCH_2D$ and the trimethylaluminium used in these experiments contained <0.02 mole % Et groups.

1.1.11 Known Organo-silyl and -Germyl Main Group Complexes

(a) Group I

Alkali metal compounds of the type $R_3M'M$ (M' = Ge,Si) have been previously discussed in sections 1.1.5 and 1.1.9. They are usually generated by cleavage of R_6M_2 or R_3MX compounds (X = Ph,Cl) with the alkali metal, and the R_3M^- anion is always more stable when at least one R group is aryl. Stable trialkylgermyl anions can be generated by the cleavage of hexaalkyldigermanes and trialkylgermyl halides using potassium or lithium in hexamethylphosphorotriamide.[43] This is a convenient method although separation of the final products from the high boiling solvent can sometimes be difficult.

No $R_3M'M$ compounds have been isolated and no information exists as to their state of association or solvation.

An alternative method for producing Ph_3GeLi is to react butyl-lithium with triphenylgermane[53] (34).

$$Ph_3GeH + Bu^nLi \longrightarrow Ph_3GeLi + Bu^nH \qquad (34)$$

Some butyltriphenylgermane is formed.

This reaction is in contrast to that between triphenylsilane and butyl-lithium (35).

$$Bu^nLi + Ph_3SiH \longrightarrow Ph_3SiBu^n + LiH \qquad (35)$$

which yields high amounts of the tetrasubstituted silane[54].

This difference in reaction can possibly be attributed to the different electronegativities of Si and Ge.

A third method of synthesising the R_3M anion is to use the $(R_3M)_2Hg$ compounds and react them in lithium with T.H.F. Various derivatives require different times, for whereas $(Me_3Ge)_2Hg$ and lithium react in T.H.F. in one hour at 20°,[55,56] $(Me_3Si)_2Hg$ and lithium requires at least four hours in refluxing T.H.F.[57] This point will be discussed more fully in 1.2.2. The triethylgermyl-lithium anion can also be generated by stirring bistriethylgermylmercury with lithium shot in benzene for three days.[58]

(b) Group IIA

There have been no reports of definite beryllium-silicon or -germanium complexes, although addition of triphenylgermyl-lithium to beryllium chloride leads to a polymeric phenyl germane which contains some beryllium.[59]

Organosilyl- and germyl complexes of magnesium however, have been demonstrated to be present in many reactions[8,27], although none have been isolated or obtained free of other compounds (usually donor solvents).

These "Grignard" type compounds are the cause of disilanes and germanes being formed along with higher homologues (36).

$$R_3MX + Mg \longrightarrow R_3MMgX$$

$$R_3MMgX + R_3Mx \longrightarrow R_6M_2 + MgX_2 \qquad (36)$$

Bistriphenylsilyl derivatives of calcium, strontium and barium have been made by reacting the metal with Ph_6Si_2 in liquid ammonia[46] (37).

$$Ph_6Si_2 + M \xrightarrow{NH_3} (Ph_3Si)_2M \qquad (37)$$

The calcium and strontium derivatives are solvolysed rapidly by the liquid ammonia but the strontium compound has been isolated and its properties and reactions studied. It is a yellow compound rapidly hydrolysed to Ph_3SiH and Ph_3SiOH and decomposes at 160° to give phenyl polysilanes.

No calcium complex of germanium has yet been made although both strontium and barium cleave hexaphenyldigermane in liquid ammonia giving finally T.H.F. complexes which decompose at 40°.[60] (38).

$$Ph_6Ge_2 \xrightarrow{Sr,NH_3} (Ph_3Ge)_2Sr \xrightarrow{T.H.F.} (Ph_3Ge)_2Sr\,.\,(T.H.F.) \qquad (38)$$

Group IIB

Zinc, cadmium and mercury form relatively stable complexes with silicon and germanium and several compounds have been isolated. They are all air, moisture and to some extent light sensitive.

Bistriphenylsilylzinc, formed from Ph_3SiK and zinc chloride in liquid ammonia has been isolated and its reactions studied[46].

It is similar in its properties to its strontium analogue and decomposes above 105° with formation of phenyl-polysilanes.

Bistriethylgermylzinc is formed by reacting Et_3GeLi with $ZnCl_2$ in

T.H.F.[61] (39).

$$(Et_3Ge)_2Hg + 2Li \longrightarrow Et_3GeLi \xrightarrow{ZnCl_2/T.H.F.} (Et_3Ge)_2Zn \qquad (39)$$

It is an involatile yellow-green oil which reacts with EtBr to form Et_4Ge and $ZnBr_2$. The reaction between triethylgermane and diethylzinc however results in a polymeric zinc containing compound.[2] (40)

$$nEt_2Zn + nEt_3GeH \longrightarrow EtH + Et_4Ge + Zn + Et_3GeZn(GeEt_2)_nZnGeEt_3 \qquad (40)$$

The reactions between the germyl metallics, GeH_3K and Ph_3GeK with zinc, cadmium and mercuric chlorides go in a similar way[62]. (41)

$$R_3GeK + MCl_2 \xrightarrow[-20^o]{T.H.F.} K\,M(GeR_3)_2Cl_2 \cdot T.H.F. \xrightarrow{\Delta H \text{ or adding toluene}} M(GeR_3)_2 \qquad (41)$$

yielding first a solvent-stabilised complex which is then decomposed by heat or replacing the solvent, to form the digermyl-metal complex. Bistriethylsilylcadmium[62], bistriethylgermylcadmium[63] and bistriphenylgermylcadmium[64,65] have all been made by the general reaction (42).

$$2R_3M'H + Et_2Cd \longrightarrow (R_3M')_2Cd + 2EtH \qquad (42)$$

These compounds are all decomposed on heating at 100-150° with formation of cadmium and the hexaorganodisilane or digermane.

The group IVb mercury compounds have been the subject of a number of papers and their use in synthetic chemistry is increasing. The trimethylsilyl and trimethylgermyl derivatives have been made by the reactions[46,66,67]. (43)

$$\begin{matrix} R_3GeH + Et_2Hg \\ \\ R_3GeX + Hg/Na \end{matrix} \searrow\nearrow (R_3Ge)_2Hg \qquad (43)$$

Bis(trimethylsilyl)mercury cannot be formed using trimethylsilane and diethylmercury, probably due to the high energy of the Si-H bond combined with the Hg-C bond in Et_2Hg. A recent paper describes the use of di-t-butylmercury[68] instead of diethylmercury and this is the best method of making the higher alkyl derivatives. The best method of making the lower alkyl derivatives is to shake 1% sodium amalgam with Me_3SiCl/ Me_3GeBr under argon for two or three weeks in a "rotaflo" single necked flask[69] (see 1.3.2).

The lower trialkyl derivatives are extremely air-sensitive and have been known to spontaneously ignite in air[69]. They sublime readily and have a similar smell to dimethylmercury.

Their chemistry has been reviewed[70,71] and typical reactions are (44)[46] and (45)[2].

$$(Me_3Si)_2Hg + HCl \longrightarrow Me_3SiCl + Me_3SiH + Hg \qquad (44)$$

$$2(Me_3Ge)_2Hg + O_2 \longrightarrow 2(Me_3Ge)_2O + 2Hg \qquad (45)$$

In most of the reactions mercury is formed. Other properties including spectra, will be more closely examined in section 1.2 of this thesis. There has been a little controversy about the mechanisms of the reactions of bistrimethylsilylmercury[72], whether it reacts by a molecular or free radical mechanism. In view of the weakness of the Hg-Si bond and the general susceptibility of the compound to sunlight, differences between the mechanisms will be marginal.

Some interesting compounds are formed from the irradiation of trichlorosilane and a dialkyl mercury[72] (46).

$$HgR_2 + 2SiHCl_3 \xrightarrow{h\nu} 2RH + (Cl_3Si)_2Hg \qquad (46)$$

The bis(trichlorosilyl)mercury compounds are used in the synthesis of unsymmetrical group IVb compounds (47).

$$Hg(SiCl_3)_2 + HGeCl_3 \longrightarrow HSiCl_3 + Cl_3Si\text{-}GeCl_3 + Hg \qquad (47)$$

Group III

Comparatively little work has been done on group III. Several boron-silicon complexes are known[73], for example trimethylsilylbisdimethyl-aminoborane $Me_3SiB(NMe_2)_2$ (48).

$$Me_3SiLi + (Me_2N)_2BCl \xrightarrow{LiCl} Me_3SiB(NMe_2)_2 \qquad (48)$$

$$Me_3SiCl + 2K + (Me_2N)_2BCl \xrightarrow{-2KCl} Me_3SiB(NMe_2)_2$$

A similar boron-germanium compound was obtained from bisdimethyl-aminoboronchloride and germyl potassium[74] (49).

$$(Me_2N)_2BCl + KGeH_3 \xrightarrow{-60^{\circ}} (Me_2N)_2BGeH_3 \qquad (49)$$

Both of the above compounds are air- and water-sensitive. Apart from compounds similar to the ones above, i.e. with at least one dialkylamino group in the boron atom, no other sort of boron-silicon compound has been isolated. However there are plenty of anionic or solvent-stabilised complexes. For example triphenylgermyl-lithium reacts with triphenylborane (50)[75].

$$Ph_3B + Ph_3GeLi \longrightarrow Li[Ph_3GeBPh_3] \xrightarrow{Me_4NCl} Me_4N^+[Ph_3GeBPh_3]^- \qquad (50)$$

Only one aluminium compound of silicon and germanium has been

characterised and that is the silyldibutylalane. [74] (51).

$$Bu_2AlCl + KSiH_3 \xrightarrow[\text{diglyme}]{-60^\circ} K^+\left[Bu_2AlSiH_3Cl\right]^- \xrightarrow{140^\circ} Bu_2AlSiH_3 \qquad (51)$$

This complex is an oily liquid, air-sensitive but stable to heat. No molecular weight data were given. An aluminium-germanium complex is said to be formed by reacting $LiAlH_4$ with GeH_4 [76] (52).

$$AlH_4^- + GeH_4 \xrightarrow[20^\circ]{\text{T.H.F.}} H_2 + \left[H_3Al\text{-}GeH_3\right]^- \qquad (52)$$

but has not been isolated, as on removal of solvent a polymeric residue is left.

Recently two gallium-germanium complexes have been made by E. Amberger[77] by reacting germyl-potassium and triphenylgermylpotassium with dimethyl-gallium chloride (53).

$$Ph_3GeK + Me_2GaCl \xrightarrow{\text{T.H.F.}} K\left[Me_2GaClGePh_3\right] \xrightarrow{\text{Toluene}} Me_2GaGePh_3$$
$$H_3GeK + Me_2GaCl \xrightarrow{\text{T.H.F.}} K\left[Me_2GaClGeH_3\right] \longrightarrow Me_2GaGeH_3 \qquad (53)$$

The Me_2GaGeH_3 complex slowly decomposes at 60° with loss of GeH_2 forming Me_2GaH (54).

$$Me_2GaGeH_3 \longrightarrow Me_2GaH + (GeH_2)_n \qquad (54)$$

The compounds $(Et_3Ge)_3Ga$ and $(Et_3Ge)_2GaEt$ have been reported but no experimental details have been given[70].

Only one silicon-indium compound has been prepared, tristrimethyl-silylindium[78] from trimethylchlorosilane, lithium metal and indium trichloride at -30° (55).

$$InCl_3 + 3Me_3SiCl + 6Li \xrightarrow{T.H.F.} (Me_3Si)_3In + 6LiCl \qquad (55)$$

This compound is very unstable and the greenish yellow crystals decompose under a vacuum above 50^o in the dark and above 0^o on exposure to daylight producing In and Me_6Si_2. A band at 311 cm^{-1} has been tentatively assigned to ν(In-Si).

Tristriethylgermyl, and -silylthallium have been made from reacting triethylthallium with the triethylgermane and silane[79] (56).

$$3Et_3MH + Et_3Tl \xrightarrow{100^o} (Et_3M)_3Tl \qquad (56)$$

The germanium derivative is thermally very stable and its reactions with several compounds are shown (57).

$$(Et_3Ge)_3Tl \begin{cases} \xrightarrow{Hg\ 20^o} (Et_3Ge)_2Hg \\ \xrightarrow{C_2H_4Br_2} C_2H_4 + TlBr + Et_3GeBr \\ \xrightarrow{Et_3SnH} Et_3GeH + Et_6Sn_2 + Tl \end{cases} \qquad (57)$$

Tristrimethylgermylthallium has been made by reacting trimethylthallium with $(Me_3Si)_2Hg$[80] (58).

$$3(Me_3Si)_2Hg + 2Me_3Tl \longrightarrow (Me_3Si)_3Tl + 3Me_2Hg \qquad (58)$$

It is a blood-red solid, unstable at 20^o and its Raman spectra has been investigated[81]. Typical reactions are (59).

$$(Me_3Si)_3Tl \begin{cases} \xrightarrow{HI} (Me_3Si)_2TlI + Me_3SiH \\ \xrightarrow{HCN} 2Me_3SiH + Me_3SiCN + TlCN \end{cases} \qquad (58)$$

Group IV

Metal-metal bonded compounds within group IV have received the

attention of several reviews[5,6,7,70] and it is not proposed to discuss them here.

Group V

Arsenic-silicon bonds may be made by reacting dimethylarsinyllithium with trimethylchlorosilane[82] (60).

$$Me_2As^-Li^+ + Me_3SiCl \longrightarrow LiCl + Me_2As\text{-}SiMe_3 \qquad (60)$$

No germanium-arsenic compounds have yet been made but germanium and silicon antimony complexes may be made by the reaction[83] (61).

$$Sb + 3Li \xrightarrow{NH_3} Li_3Sb \xrightarrow{Me_3MCl} (Me_3M)_3Sb \qquad (61)$$

The germanium- and silicon-bismuth complexes may be made by the general reaction[84] (62).

$$3R_3MH + R'_3Bi \longrightarrow 3R'H + (R_3M)_3Bi \qquad (62)$$

All of the group V silicon and germanium complexes are air-, water- and light-sensitive.

1.2 Discussion

The discussion in this section is concerned with attempts to synthesise and isolate compounds containing either aluminium-silicon or-germanium bonds. In no case has a stable compound been isolated. Some experiments aimed at establishing aluminium-silicon or -germanium bonds produced, rather surprisingly, no reaction. Other approaches gave reaction products which could be accounted for if reactive aluminium-silicon or germanium complexes had been produced as reactive intermediates.

In a few cases evidence (not entirely convincing) has been obtained for impure aluminium-silicon complexes such as $(Me_3Si\text{-}AlMe_2)$(T.H.F.) and $(Me_3SiAlCl_2)_n$ and for impure aluminium-germanium, complexes such as $(Me_3Ge)_3Al$ and $Me_3AlGeCl_3$.

1.2.1 Reactions of the type $R_2AlR' + R_3"MH$

(a) $R_3"SiH$

The attempted reactions between trialkyl- and triaryl-silanes and trialkylaluminium compounds are listed in Fig 2(a).

As no significant quantities of alkane were formed and starting materials were recovered the reactions (1) and (2) did not occur under the conditions used.

$$R_2AlR' + R_3"SiH \begin{cases} \not\rightarrow R_2Al\text{-}SiR_3" + R'H & (1) \\ \not\rightarrow R_2AlH + R_3"SiR' & (2) \end{cases}$$

This non-reactivity can possibly be attributed to:(a) steric factors making the probable penta-co-ordinate transition state unfavourable on entropy grounds and the final product unstable, and (b) insufficient proton character of the silyl-hydrogen. No significant difference in

Fig. 2(a)

$R_2AlR' + R_3''SiH$

R	R'	R''	Temperature	Products
Me	Me	Me	20^o, 60^o	——
Me	NMe_2	Me	60^o	——
^iBu	H	Me	110^o	——
Me	Me	Ph	20^o	——
Me	Me	C_6F_5	60^o	——
^iBu	H	C_6F_5	70^o	——

Fig. 2(b)

$R_2AlR' + R_3''GeH$

R	R'	R''	Temperature	Products
Me	Me	Me	110^o	——
Et	Et	Et	90^o, 160^o	4.8% C_2H_4
^iBu	H	Me	110^o	9.6% H_2
^iBu	H	Et	110^o	6.95% H_2
Me	Me	Ph	20^o	——
Me	Me	Cl	20^o	13.2% CH_4, 28% Me_3GeH, Me_2GeHCl, $MeGeHCl_2$

reactivity was found in donor solvents and so factors involving the energy required to break the alkyl-bridge in the trialkyl aluminium compounds cannot be important.

The polarisation of the Si-H bond made seemingly little difference in reactivity either, as $(C_6F_5)_3SiH$ and $(C_6H_5)_3SiH$ also did not react. Thus the probable deciding factor in the above type of reaction is the steric hindrance of the transition state, linked with the chemical stability of the final products. It is worth noting that the only aluminium-silicon characterised compound is $nBu_2Al\text{-}SiH_3$, which has a relatively small group attached to the aluminium atom and formed using an ionic reaction[74]. The only donor-free boron-silicon compounds known, are those with dimethylamino groups on the boron-atom, e.g. $Me_3Si\text{-}B(NMe_2)_2$[73], in which the B-Si bond is presumably stabilised by interaction between empty p orbitals on the nitrogen and boron atoms. An attempt to make an equivalent compound $Me_3Si\text{-}AlMe(NMe_2)$ using the above type of reaction met with no success.

(b) $R_3"GeH$

These reactions are listed in Fig. 2(b) with generally similar results, (3) and (4).

$$R_2AlR' + R_3"GeH \begin{cases} \not\rightarrow R_2Al\text{-}GeR_3" + R'H & (3) \\ \not\rightarrow R_2AlH + R_3"GeR' & (4) \end{cases}$$

It can be seen that even the less hydridic nature of the germyl-proton does not affect the reactivity. It is interesting that whereas triethylthallium and triethylgermane and -silane react at 100° (5)[79],

$$3Et_3GeH + Et_3Tl \xrightarrow{100^\circ} (Et_3Ge)_3Tl + 3EtH \qquad (5)$$

the equivalent reaction involving tri-ethylaluminium only produces some ethylene from pyrolysis of the aluminium compound. Presumably the existence of stable lower valent thallium species, weaker thallium-carbon bond strength and the larger size of the thallium atom must contribute to this difference in reactivity.

However trichlorogermane and trimethylaluminium react quickly at 20° forming aluminium chloride, methane, trimethylgermane and methylchlorogermanes (6).

$$Me_3Al + HGeCl_3 \xrightarrow{20^\circ} CH_4,\ Me_3GeH,\ MeGeH_2Cl,\ Me_2GeHCl,\ MeGeHCl_2 \text{ and } AlCl_3 \quad (6)$$

The methane could possible be formed from (7) and/or (8),

$$Me_3Al + HGeCl_3 \longrightarrow (Me_2Al\text{-}GeCl_3) + CH_4 \quad (7)$$

$$HGeCl_3 \longrightarrow GeCl_2 + HCl \longrightarrow CH_4 + Me_2AlCl \quad (8)$$

although reaction (7) is more unlikely, as no evidence of a germanium-aluminium complex was found. As a fair amount (30%) of trimethylgermane was made, straight methylation of the trichlorogermane must occur presumably with a similar mechanism to the alkylation of $GeCl_4$ (9).

$$2Me_3Al + 2HGeCl_3 \longrightarrow 2Cl_2GeH(Me) + (Me_2AlCl)_2 \quad (9)$$

$$\downarrow$$

$$HGeCl_3 \text{ etc.}$$

A final point on the reactions between alkylaluminium compounds and the Group IVb hydrides is that triethylstannane and diethylberyllium react to form methylberyllium hydride and tetraethylstannane[85] (10).

$$Et_3SnH + Et_2Be \xrightarrow[4 \text{ hours}]{75^\circ} Et_4Sn + EtBeH \quad (10)$$

whereas no reaction was detected between triethylaluminium and trimethyl-

stannane after 12 hours at 60°.

1.2.2 Reactions involving Anionic Silicon/Germanium Species

(i) Trimethylsilyllithium and dimethylaluminium chloride

Dimethyl(trimethylsilyl)aluminium had been reported as being formed in the reaction between dimethylaluminium hydride and bistrimethylsilylmercury[46]. Although it was stated to be unstable, it was decided to attempt to stabilise the complex using a strong donor solvent, T.H.F. The first stage in the reaction was to generate the Me_3Si species by reacting lithium shot with $(Me_3Si)_2Hg$ in T.H.F.[57] and then adding $(Me_2AlCl)_2$ to the Me_3SiLi solution (11).

$$(Me_3Si)_2Hg + 2Li \xrightarrow[\text{reflux}]{\text{12 hours}} 2Me_3SiLi \xrightarrow{(Me_2AlCl)_2} Me_2AlSiMe_3$$

The $Me_2AlSiMe_3$ complex could also presumable exist in a complex with lithium chloride, i.e. $Li^+[Me_2AlSiMe_3Cl]^-$.

The trimethylsilyllithium was generated and its chocolate-brown colour was destroyed by addition of the aluminium compound. However on working up the reaction mixture, a yellow solid was always obtained together with various viscous liquids. The yellow solid was positively identified as bistrimethylsilyl mercury from its p.m.r. (τ = 9.61) and far infra-red spectrum with ν(Hg-Si) at 315.4 cm^{-1}. (Literature value 318 cm^{-1}).[46]

The literature method[57] of preparing Me_3SiLi is to reflux $(Me_3Si)_2Hg$ with Li shot for four hours and decant.

No mercury was seen on hydrolysis and the Me_3SiLi moiety was characterised by addition of PhBr resulting in a 10% yield of Me_3SiPh. However the above do not necessarily confirm the presence of Me_3SiLi and the absence of $(Me_3Si)_2Hg$ as experimentally it was found that $(Me_3Si)_2Hg$ was only slowly decomposed by water (in the absence of oxygen) and the low yield of Me_3SiPh could also be obtained from reaction (12).

$$(Me_3Si)_2Hg + PhBr \longrightarrow Me_3SiPh + Me_3SiBr + Hg \qquad (12)$$

The stability of $(Me_3Si)_2Hg$ in the presence of $(Me_2AlCl)_2$ was confirmed by a later experiment which showed no reaction between the two compounds after 48 hours at 20°. Hence the initial formation of Me_3SiLi did not go to completion. The reaction produced however on fractionation, liquids containing Me-Si and Me-Al groups (from p.m.r.) as well as some Me_4Si (identified by v.p.c.). Hydrolysis of these liquids produced Me_3SiH (indicative of an Al-Si bond) and CH_4, as well as free T.H.F., although not in the quantities required for $[Me_3SiAlMe_2]$ and $[Me_3SiAlMe_2$ T.H.F.$]$. (See below).

Hydrolysis products	Involatile at 80°	Involatile at 0°	$Me_3SiAlMe_2$	$Me_3SiAlMe_2$ T.H.F.
CH_3 wt%	5.96	15.7	18.2	14.8
CH_3Si wt%	27.94	21.17	56.1	36.1

It can be seen that the involatile at 80° fraction is richer in $SiMe_3$ groups than the involatile at 0° fraction.

This is compatible with an aluminium-silicon complex being formed and decomposing to some extent on heating and pumping, to form higher methylpolysilanes and trimethylaluminium. Hence the reaction is postulated to proceed as in (13),

$$Me_3SiLi + (Me_2AlCl)_2 \longrightarrow Me_3Si\text{-}AlMe_2 \text{ (T.H.F.)} \xrightarrow{80^\circ} Me_{2n+2}Si_n + Me_3Al \cdot \text{T.H.F.} \qquad (13)$$

the complex decomposing by Me_2Si: elimination and methyl transfer.

(ii) Trialkylgermyl anions

Initially attempts were made to generate the trialkylgermyllithium species in hexamethyltriphosphoramide. The orange colour of the R_3GeLi was immediately discharged on addition of the aluminium halide but the products could not be studied owing to the involatility of the solvent. Triethylgermyllithium was generated in benzene by stirring for three days with Li shot[58] (14)

$$(Et_3Ge)_2Hg + 2Li \longrightarrow 2Et_3GeLi + Hg \qquad (14)$$

and reacting this with $(Me_2AlCl)_2$ resulted in the formation of a good yield of Et_8Ge_3, Et_6Ge_2 and a smaller amount of $MeGe_2Et_5$ (mass spectrometry). Presumably the mechanism involves an aluminium-germanium intermediate which disproportionates and reacts further as in (15) by alkyl exchange, coupling and Et_2Ge: formation.

$$Et_3GeLi + Me_2AlCl \xrightarrow[C_6H_6]{20^\circ} LiCl + [Et_3Ge\text{-}AlMe_2] \longrightarrow Et_8Ge_3,\ Et_6Ge_2 \text{ and } Et_5Ge_2Me \qquad (15)$$

(iii) Triphenylgermyllithium and dimethylaluminium chloride

Triphenylgermyllithium was generated from triphenylgermane and butyllithium, and reacted with dimethylaluminium chloride. The reaction produced a white chloride-free solid containing Ph-Ge, Me-Al and Et_2O (from p.m.r.) and a liquid residue which contained triphenylgermane and methylaluminium compounds (infra-red and p.m.r.).

The white solid gave on hydrolysis only 20% of the methane required for the formulation $Ph_3Ge\text{-}AlMe_2Et_2O$. Presumably the complex is unstable and decomposes into insoluble polymeric phenylgermanes along with soluble methyl-aluminium compounds, thus reducing the methane produced on hydrolysis.

Similar products were obtained from the reaction between triphenylgermyllithium and beryllium chloride etherate[59].

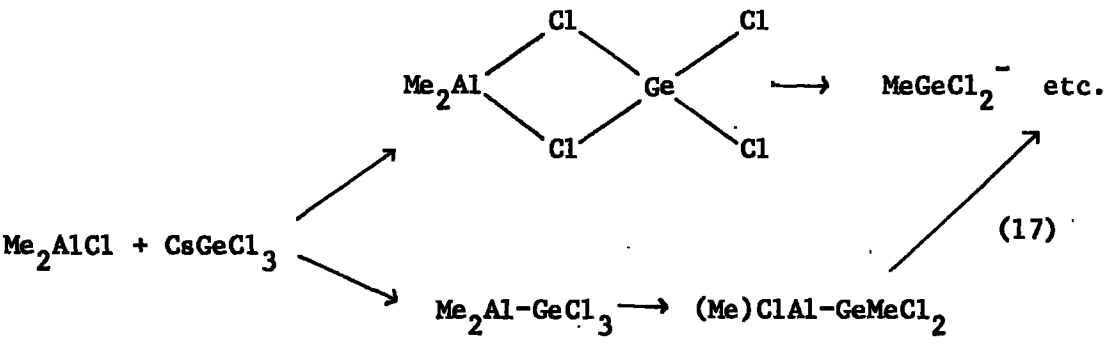
(iv) Caesium trichlorogermanite and dimethylaluminium chloride

The attempted formation of dimethyl(trichlorogermyl)aluminium from caesium trichlorogermanite and dimethylaluminium chloride resulted in the formation of methyl-polygermanes, chloromethylpolygermanes and aluminium chloride (16).

$$2CsGeCl_3 + (Me_2AlCl)_2 \longrightarrow Me_{16}Ge_7,\ Me_{12}Ge_5 + \text{higher homologues} + \text{chlorinated species} + AlCl_3 \qquad (16)$$

No lower methylgermanes were detected and the large Me_3Ge^+ peak observed in the mass spectrum is indicative of chain branching.

The reaction goes possibly either via an Al-Ge intermediate and then halogen-methyl exchange or by preliminary methylation of the $GeCl_3$ anion followed by polymerisation (17).



1.2.3 Reactions Involving Germyl- and Silylmercury compounds

(i) Aluminium metal and bistrimethylgermylmercury

The reaction between bistrimethylgermylmercury and aluminium metal went smoothly at 20° over 72 hours producing mercury, methylpolygermanes and trimethylaluminium (p.m.r.) (18).

$$(Me_3Ge)_2Hg + Al \xrightarrow{\text{hexane}} Me_{2n+2}Ge_n + Hg + Me_3Al \qquad (18)$$

The analogous reaction with bistrimethylsilylmercury[46] requires a temperature of 70°, at which temperature, decomposition of the $(Me_3Si)_2Hg$ into Me_6Si_2 and mercury also becomes apparent.

The mechanism of the reaction must proceed via an aluminium-germanium intermediate (19, 20 and 21) which breaks down as shown, with a similar mechanism to that postulated by Wiberg[46].

$$3(Me_3Ge)_2Hg + 2Al \longrightarrow 2Al(Me_3Ge)_3 + 3Hg \qquad (19)$$

$$Al(GeMe_3)_3 \longrightarrow AlMe_3 + :GeMe_2 \qquad (20)$$

$$Me_2Ge: + (Me_3Ge)_2Hg \longrightarrow Me_3Ge-GeMe_2-Hg-GeMe_3 (I)$$

$$\swarrow \qquad \searrow$$

$$Hg + Me_8Ge_3 \qquad :GeMe_2 \text{ etc.} \qquad (21)$$

The "chain-growing" step is reaction (21).

As the highest methylpolysilane isolated in the silylmercury reaction was $Me_{10}Si_4$ and as methylpolygermanes up to $Me_{14}Ge_6$ were identified, it seems that the intermediate I must be more stable than the analogous silicon complex.

(ii) Bistrimethylsilylmercury and di-isobutylaluminium hydride

No reaction was detected between $^{i}Bu_2AlH$ and $(Me_3Si)_2Hg$. This has been confirmed by other work[72]. Dimethylaluminium hydride however reacts with $(Me_3Si)_2Hg$ smoothly at 20° forming trimethylaluminium and methylpolysilanes[46] (22).

$$Me_2AlH + (Me_3Si)_2Hg \longrightarrow Me_3SiH + Me_3Al + Hg + Me_{10}Si_4 + Me_8Si_{13} + Me_6Si_2 \qquad (22)$$

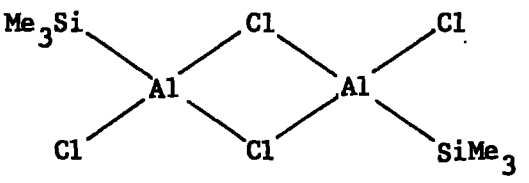
This difference in reactivity is possibly ascribed to steric hindrance by the bulky iso-butyl groups as the difference in association energies of the bridging hydrogens in the two compounds is not significant, each bridge being about 15-20 kcal.mol^{-1} [86].

(iii) Bistrimethylsilylmercury and aluminium trichloride

The reaction goes rapidly at 20° in benzene solution, mercury is precipitated and Me_3SiCl formed. The reaction can be postulated to proceed initially at least as (23).

$$2(Me_3Si)_2Hg + Al_2Cl_6 \xrightarrow{20^\circ} 2Me_3SiCl + Hg + (Me_3SiAlCl_2)_2 \qquad (23)$$

The infra-red spectrum of the residue showed Si-CH_3 bonds as well as ν(Al-Cl), both terminal and bridging. A large band was also noted at 225 cm^{-1}. No halogen-methyl exchange occurs as the p.m.r. spectrum only shows a multiplet around 9.65τ and no methane or trimethylsilane are produced on hydrolysis. Treatment of the residue with 1,2-dibromoethane produced no ethylene. The initial complex is formulated as:



and presumably some decomposition occurs with the formation of methylpolysilanes.

It is interesting that the replacement of two chlorine atoms by methyl groups on the aluminium chloride produces no reaction with bistrimethylsilylmercury at 20° (24).

$$2(Me_3Si)_2Hg + (Me_2AlCl)_2 \longrightarrow \text{no reaction} \qquad (24)$$

Possibly the energy required to break the chlorine bridge is too great.

1.2.4 Alkylation of Triphenylphosphine-germanium-di-iodide using Trialkylaluminium Compounds

Triphenylphosphine reacts with germanium di-iodide on refluxing in a hydrocarbon solvent at 130° to form a biscuit-coloured, highly air-sensitive compound, Ph_3PGeI_2, in which the germanium atom is nominally three co-ordinate[87].

The purpose of these reactions was to see if the three co-ordinate germanium compound was alkylated in a different way from the other germanium halides, e.g. to form cyclic alkylpolygermanes.

Cyclic alkylpolygermanes have been relatively little studied and have been produced in only one reaction [33](25).

$$Me_2GeCl_2 \xrightarrow{Li,\ T.H.F.} (Me_2Ge)_6 + \text{higher polymers} \qquad (25)$$

Trimethylaluminium reacted with the Ph_3PGeI_2 complex in benzene solution on stirring for 72 hours at 20° and refluxing for 12 hours.

A small amount of brown precipitate was obtained which contained P, C, H and I but no germanium and is probably polymeric oxide material. Hydrolysis of the pale green reaction mixture produced an alkyl-phosphine-like smell and it was wondered if Me_3Al could have alkylated Ph_3P under the conditions used.

It was established that trimethylaluminium and triphenylphosphine combine to give the adduct, Ph_3PAlMe_3, which was completely characterised by analysis, hydrolysis and p.m.r. spectrum. Reaction in refluxing benzene and stirring for one week gave the same adduct. The phosphine-like smell was probably due to Ge-P bonded by-products.

Separation of the methyl-polygermanes from the residual triphenyl-

phosphine and triphenylphosphine oxide proved difficult and eventually a partial separation was achieved by micro-cup distillation and ordinary vacuum distillation ($130^{o}/10^{-3}$mm. Hg).

The more volatile fraction was shown to be mainly $Me_{10}Ge_4$ and Me_8Ge_3. Much smaller amounts of $Me_{16}Ge_7$, $Me_{14}Ge_6$ and $Me_{12}Ge_5$ were detected using mass spectrometry and p.m.r.

The residue consisted of triphenylphosphine along with triphenylphosphine oxide, with substantial amounts of $Me_{16}Ge_7$, $Me_{12}Ge_5$, $Me_{10}Ge_4$ and methyl germanium oxides together with trace amounts of unidentified higher polymers. No cyclic methylpolygermane molecular ion was seen in the mass spectrum.

$$Me_3Al + Ph_3PGeI_2 \longrightarrow Me_8Ge_3 + Me_{10}Ge_4 + Me_{12}Ge_5 + Me_{14}Ge_6 + Me_{16}Ge_7$$
$$+ \text{higher oligomers} + \text{cyclic oxides}$$

Since Ge(IV) compounds have been produced from Ge(II) compounds an oxidation has occurred. Presumably the mechanism is similar to that of Me_3Al/GeI_2 with the probability that the triphenylphosphine present could stabilize the lower valent aluminium or germanium compounds.

Various mechanisms can be formulated, generally involving reactive $GeMe_2$, GeI_2 or Al-Ge species.

Formation of Ge-Ge bonds could arise from insertion reactions by the $:GeMe_2$ species (27).

$$Ph_3PGeI_2 + Me_3Al \longrightarrow :GeMe_2 + MeAlI_2 + Ph_3P$$
$$\downarrow$$
$$Me_3Ge\text{-}AlI_2 \qquad (27)$$
$$\swarrow$$
$$Me_3GeGeMe_2\text{-}AlI_2 \quad :GeMe_2$$

Chain branching could occur via partially methylated germanium species

such as in (28).

$$Ph_3PGeIMe + Me_3GeAlI_2 \xrightarrow{MeGeI} Me_3Ge\text{-}\underset{Me}{\overset{I}{Ge}}\text{-}AlI_2 \xrightarrow{:GeMe_2} Me_3Ge\text{-}GeMe_2\text{-}AlI_2GeMe_2I \quad \text{etc.} \qquad (28)$$

The absence of any detectable cyclic compounds is quite puzzling because of the postulated presence of $:GeMe_2$ moieties.

Possibly the loss of entropy and thermodynamics (and in particular) of the cyclisation process is not favoured under the mild conditions used whereas chain branching and lengthening is a favourable process.

The reaction between triethylaluminium and Ph_3PGeI_2 went in a similar fashion to the trimethylaluminium reaction, although no precipitate was obtained this time. Separation of the products was a little easier by distillation, as the volatile ethylgermanes were Et_8Ge_3 and Et_6Ge_2 (p.m.r., mass spectroscopy and infra-red) and the volatile residue consisted of Ph_3P, Ph_3PO and $Et_{10}Ge_4$, Et_8Ge_3 with other cyclic oxides. No cyclic polygermanes or higher polymers were detected and the shorter chain length was possibly due to steric hindrance by the ethyl groups in the alkylation process (29).

$$Et_3Al + Ph_3PGeI_2 \longrightarrow Et_{10}Ge_4,\ Et_8Ge_3 + Et_6Ge_2 + \text{cyclic oxides} \qquad (29)$$

Thus the reactions between Me_3Al, Et_3Al and Ph_3PGeI_2 produced similar products to the equivalent AlR_3/GeI_2 reactions, although no alkyl chain lengthening was detected with Me_3Al/Ph_3PGeI_2.

1.3 Experimental

1.3.1 General Handling Techniques

The general handling techniques described below are relevant to the experimental sections in the other parts of this thesis. Unless otherwise stated all experiments were performed under a nitrogen atmosphere (B.O.C. "White spot") purified by either passing through a copper catalyst B.T.S. at 170° to remove oxygen or by passing through a molecular sieve.

Manipulations that could not be carried out under nitrogen on the bench, were carried out in a nitrogen-filled glove box. The glove box was fitted with a circulating pump and when not in use the nitrogen was passed through two copper towers at 380° and two liquid nitrogen traps. When necessary the oxidised copper was regenerated by passing a stream of hydrogen through the columns at 120°. The glove box had in addition to the normal entry port, a small evacuable one for quick entry. It also contained a single pan electric balance for analytical data.

Conventional vacuum lines were used throughout this work. They consisted generally of three main sections, a fractionation train, a Töpler pump and a storage system of cold fingers and three-litre bulbs.

For fractionating gases and liquids on the vacuum line the following cold traps were used:

-78°	Acetone/solid CO_2
-96°	Toluene/liquid N_2
-112°	Ethanol/liquid N_2
-126°	Methylcyclohexane/liquid N_2
-155°	See ref. 88.
-196°	Liquid N_2

1.3.2 Preparation and Purification of Starting Materials

Me_3Al, Et_3Al, $^iBu_3Al$

These were available in the laboratory from the Ethyl Corporation.

$AlCl_3$

This was made by burning pure aluminium in chlorine diluted by nitrogen, subliming the aluminium chloride into a receiver, and storing in a glove box.

Me_2AlCl

This was made by carefully mixing stoichiometric amounts of $AlCl_3$ and Me_3Al in a cooled vessel.

$^iBu_2AlH$

This was made by heating 30 ml. of $^iBu_3Al$ at 140° for two hours. When isobutene evolution had finished the distillation apparatus was evacuated and $^iBu_2AlH$ distilled over $90°-110°/10^{-3}$mm. The product was redistilled and its isobutyle to hydrogen ratio checked by hydrolysis.

Me_3SiH

This was synthesised by refluxing chlorotrimethylsilane and $LiAlH_4$ in dioxan , collecting in a -78° trap and completing the fractionation on a vacuum line .

Ph_3SiCl, Ph_3SiH

Chlorotriphenylsilane, m.p. 96° was made by the literature method from triphenylsilanol and thionyl chloride[90].

Triphenylsilane (b.p. 130°/.05 mm.) was made by reacting chlorotriphenylsilane with lithium aluminium hydride in ether[89].

$(C_6F_5)_3SiH$

This was made by adding trichlorosilane to pentafluorophenyl magnesium bromide at -12° and then refluxing for 12 hours[91]. The resulting brown solid was purified by sublimation into white crystals (80°/10^{-3} mm.) m.p. 134-136°.

R_3GeBr, R_3GeH (R = Me, Et, Ph)

The tetra-alkyl or arylgermane was made by adding one mole of germanium tetrachloride to four moles of the appropriate Grignard reagent and by either distilling out the germane or by hydrolysing and extracting with ether[92]. Me_4Ge b.p. 43°, Et_4Ge b.p. 163°, Ph_4Ge m.p. 236°.

The mono-bromosubstituted alkylgermane was made by adding the stoichiometric amount of bromine in isopropyl bromide to R_4Ge and then refluxing for three days. The bromotrialkylgermane was then separated by distillation. Me_3GeBr b.p. 114°, Et_3GeBr b.p. 191°.

Bromotriphenylgermane was made by refluxing bromine and tetraphenylgermane in ethylene dibromide for thirty minutes, distilling out the bromo-compound (206°/6 mm.) and recrystallising from benzene, m.p. 139°.[93]

The monobromo compounds were reduced by $LiAlH_4$ in ether and the R_3GeH compounds either purified by distillation or fractionation. Me_3GeH b.p. 24°, Et_3GeH b.p. 124°, Ph_3GeH m.p. 47°.

GeI_4, GeI_2

Germanium dioxide was refluxed with fresh HI (50%) for ten minutes. Most of the water was distilled off and then the residue filtered. It was then transferred to a sublimation apparatus and sublimed at 100°/10^{-3}mm. as red needles[2].

The germanium tetraiodide was then refluxed with hypophosphorous acid and more hydriodic acid until the red needles had been converted into yellow plates. The solution was filtered cold and transferred to a sublimation apparatus

where any residual GeI_4 was sublimed out[2].

$HGeCl_3$

This was made by passing hydrogen chloride gas over germanium metal, containing copper catalyst, at 400° and collecting and redistilling the resultant liquid, b.p. [illegible] 75.1°.

$CsGeCl_3$

This was made by adding $GeCl_4$ to an aqueous solution of caesium chloride and hypophosphorous acid, heating for six hours and filtering the white compound followed by exhaustive pumping.

$(R_3M)_2Hg$ R = Me, Et, M = Si, Ge

These compounds were made by the following procedure[67]. Sodium amalgam (1%) (e.g. 2g. Na in 200 g. Hg) was made up under argon in a single neck flask with a "Rotaflow" tap. The bromo- or chloro-trialkyl silane or -germane (10g.) was then added against a counter current of argon followed by cyclohexane (20-30 ml.). The flask was then attached to a shaker in a dark cupboard and shaken for two weeks. When a deep yellow colour had been formed the contents of the flask were transferred carefully to a Schlenk, filtered and the mercury washed repeatedly with cyclohexane. The cyclohexane was pumped off leaving a yellow solid which was purified by subliming ($80-100°/10^{-3}$mm.) These compounds were always stored in the dark as they were decomposed by sunlight.

1.3.3 Other Experimental Data

Solvents were purified by distillation and dried by standing over sodium or by refluxing with $LiAlH_4$. Infra-red spectra were recorded in the region 2.5-25μ in Durham on either a Grubb-Parsons G.S.2A "Spectromaster" spectrophotometer and in Belfast on a Perkin Elmer 457 grating infra-red

spectrophotometer. Solids were examined as pressed KBr discs or as Nujol mulls. Semi-solids or liquids were examined as thin films between KBr or NaCl plates. Gas spectra were recorded in gas cells with KBr or NaCl. The region 20-50μ was recorded on a Grubb-Parsons D.M. 2/DB3 instrument (in Durham) and a Grubb-Parsons D.M.4 (in Belfast).

Proton magnetic resonance spectra were recorded on a Perkin-Elmer R.10 instrument 60 MHz at 33° in Durham and Varian H.A.100 MHz at 30° in Belfast.

A variety of gas liquid chromatographs were used including the Pye 104 and the Perkin-Elmer F11. The usual conditions for the catenated organogermanes were nitrogen pressure 20 lbs.sq.in^{-1}, column temperature 200° and using an Apiezon-L column. Mass spectral investigations were carried out using an A.E.I. MS9 (Durham) and an A.E.I. MS 902 (Belfast). The fragmentation patterns of organogermanes have been discussed elsewhere (see 3.1.11) in this thesis. Calculation of isotope patterns was done either from previous publications or by a computer programme modified by Mr. A.McGregor, Chemistry Dept., Queen's University of Belfast.

Conditions employed on the mass spectra were as follows:

Electron beam voltage = 70eV, ionising beam = 100μA

Accelerating voltage = 9 kV, Source temp. = 200°

Sealed Tubes

Many experiments were performed using sealed tubes, which in most reactions were "tailor-made" for the various requirements needed. In most cases a glass-covered beaker was used and all tubes were thoroughly evacuated, dried and tested for pin holes before use.

1.3.4 Reactions using $R_2AlR' + R''_3MH$ (M = Si, Ge, Sn)

(i) Trimethylsilane and trimethylaluminium

Trimethylaluminium (0.25 ml., 0.0026M) in hexane (5 ml.) was syringed into a sealed tube and attached to a vacuum line. Trimethylsilane (35.01 Nc.c., 0.0015M) was condensed on and the tube was left at 20° for two hours. On opening 2.75 Nc.c. of methane was obtained (7% of calculated value if dimethyl(trimethylsilyl)aluminium was formed). The stoichiometric amount of Me_3SiH was recovered. The reaction was repeated at 60° and with a trace of aluminium chloride present with similar results.

(ii) Trimethylsilane and dimethylaminodimethylaluminium

Trimethylaluminium, (0.26 ml., 0.0028M) was syringed into a double break seal apparatus. The apparatus was attached to a vacuum line and 101.7 Nc.c. (0.0045M) of pure dimethylamine was condensed onto the trimethylaluminium. The apparatus was sealed off, heated in an oil bath at 110° for 45 minutes and reattached to the vacuum line. 61.31 N.c.c. (0.0027M) of methane were measured and the excess dimethylamine was pumped off leaving a white solid. Diethylether (5 ml.) was condensed onto the solid followed by 61.31 Nc.c. (0.0027M) of Me_3SiH. The tube was resealed, heated at 60° for 12 hours and on opening no methane was found. Trimethylsilane, 60.5 Nc.c. (0.0027M) was recovered and the pumped white solid was identified by its melting point, 154°, as dimethylaminodimethylaluminium.

(iii) Trimethylsilane and di-isobutylaluminium hydride

Di-isobutylaluminium hydride (0.4698 g., 0.0033M) was syringed into a break-seal apparatus, attached to a vacuum line and trimethylsilane, (62.58 Nc.c., 0.0028M) condensed on. The apparatus was sealed off and heated at 110° for 72 hours. On opening no hydrogen was detected but

59.44 Nc.c. of Me_3SiH was recovered.

(iv) Triphenylsilane and trimethylaluminium

Triphenylsilane (0.437 g., 0.0017M) was weighed out into a two-necked flask. Hexane (10 ml.) was added, and the solution was degassed. Trimethylaluminium, (16 ml., 0.0017M) was added at -196°. On standing at 20° for two hours, methane, 3.60 Nc.c. was obtained.

Formation of dimethyl(triphenylsilyl)aluminium would result in 37.67 Nc.c. of methane. The solution was pumped down and the white solid residue was identified as Ph_3SiH (infra-red).

(v) Trimethylaluminium and tripentafluorophenylsilane

Tripentafluorophenylsilane (1.6669 g., 0.0031M) was weighed out in a glove box into a double break-seal apparatus. Trimethylaluminium (0.35 ml., 0.0027M) in diethylether (7 ml.) was added at -196° and the apparatus after being degassed was sealed off. After standing for seven days at 20° it was opened and 1.94 Nc.c. of methane (I.R.) were measured. It was resealed and kept at 60° for 12 hours and 2.24 Nc.c. of methane were obtained on opening. Total volume of methane required for the formation of dimethyl(tripentafluorophenylsilyl)aluminium is 60.48 Nc.c. The solution was pumped down and the white solid residue was identified by its m.p. 134°, and infra-red spectrum as tripentafluorophenylsilane.

(vi) Di-isobutylaluminium hydride and tripentafluorophenylsilane

Tripentafluorophenylsilane (0.5855 g., 0.0029M) was weighed out into a double break-seal apparatus. Di-ethylether (5 ml.) was added and then di-isobutylaluminium hydride, (0.5208 g., 0.0036M) added at -196°. The apparatus was sealed off and heated at 60-70° for two weeks. On opening 8.71 Nc.c. of hydrogen were obtained. Formation of di-isobutyl(tripentafluorophenylsilyl)aluminium requires 66.97 Nc.c. of hydrogen. On pumping

down the residue consisted of starting material (infra-red).

(vii) Trimethylgermane and trimethylaluminium

Trimethylaluminium (0.3 ml., 0.003M) was syringed into a break-seal apparatus and benzene (5 ml.) added. Trimethylgermane (47.79 Nc.c., 0.002M) was condensed onto the trimethylaluminium and the apparatus was sealed off. It was heated at 70° for 12 hours and on opening methane, 1.34 N.c.c. was obtained. Trimethylgermane (46 Nc.c., 0.002M) was recovered and identified (infra-red).

(viii) Trimethylgermane and di-isobutylaluminium hydride

Di-isobutylaluminium hydride (0.415 g., 0.0029M) was syringed into a double break-seal apparatus. Trimethylgermane (23.72 N.c.c., 0.001M) was condensed on and the apparatus was sealed off and heated at 110° for 48 hours. On opening at -196°, 0.91 Nc.c. of hydrogen was obtained. The apparatus was resealed and heated at 110° for seven days. On re-opening at -196°, 0.56 Nc.c. of hydrogen was obtained. (Formation of di-isobutyl(trimethylgermyl)aluminium requires 23.72 Nc.c. of hydrogen).

Trimethylgermane (infra-red), 20.0 Nc.c., 0.001M was recovered from the reaction mixture and the liquid residue was identified as di-isobutyl-aluminium hydride (infra-red) ν(Al-H) 1770 cm^{-1}.

(ix) Triethylgermane and triethylaluminium

Triethylgermane (3.0 g., 0.017M) was syringed into a break-seal apparatus with a large bulb (volume about 250 ml.), degassed and frozen down to -196°. Triethylaluminium (0.56 ml., 0.005M) was added and the apparatus was evacuated and sealed off. The reaction mixture was heated at 90° for 24 hours. On opening at -78° no volatiles were obtained. The apparatus was sealed off and transferred to a glove box where an infra-red spectrum showed ν(Ge-H) at 2013 cm^{-1} and no ν(Al-H) was observed.

The experiment was repeated using similar quantities of triethylaluminium and triethylgermane. The apparatus was heated at 160° for 48 hours. On opening at 178°, ethylene (infra-red) 16.14 Nc.c. was obtained. Formation of tris-triethylgermylaluminium requires 336 Nc.c. of ethane. The infra-red spectrum of the liquid showed ν(Ge-H) at 2013 cm^{-1}.

(x) Triethylgermane and di-isobutylaluminium hydride

Triethylgermane, (0.156 g., 0·00096M) in hexane (5 ml.) was added to a double-break-seal apparatus. Di-isobutylaluminium hydride (0.3325 g., 0.0024M) was added at -196°, the apparatus was degassed, evacuated and sealed off. It was heated at 110° for 48 hours and on opening at -196°, hydrogen, 2.07 Nc.c. was obtained. Formation of di-isobutyl(triethylgermyl)aluminium requires 21.51 Nc.c. of hydrogen. The apparatus was resealed and heated at 110° for a further 48 hours. On re-opening no hydrogen was obtained.

The infra-red spectrum of the residual liquid showed ν(Ge-H) at 2010 cm^{-1} and ν(Al-H) at 1754 cm^{-1}.

The experiment was repeated using di-ethyl ether as solvent. Triethylgermane, (0.5564 g., 0.0034M) in ether (5 ml.) was added to a break-seal apparatus and di-isobutylaluminium hydride (0.4492 g., 0.0035M) was added at -196°. The apparatus was sealed off and heated at 60° for two weeks. On opening hydrogen, 5.3 Nc.c. was obtained. Required for di-isobutyl(triethylgermyl)aluminium, 76.19 Nc.c. of hydrogen. The volatiles were pumped off and ν(Ge-H) at 2010 cm^{-1} was seen in the infra-red spectrum. The residue had an infra-red spectrum nearly identical to that of di-isobutylaluminium hydride.

(xi) Trichlorogermane and trimethylaluminium

Trichlorogermane (0.46 ml., 0.005M) were syringed into a sealed tube and trimethylaluminium (0.50 ml., 0.005M) added at -196°. The tube

was sealed off and allowed to warm up to 20°. Effervescence took place and the solution turned an amber colour. A yellow solid separated out on standing for 48 hours at 20°. On opening methane, 14.80 Nc.c. (infra-red) and trimethylgermane, 31.87 Nc.c. were obtained. An infra-red spectrum of the vapour of the remaining liquid indicated ν(C-H), ν(Ge-CH_3) and ν(Ge-H).

An infra-red of the solid in perfluorokerosene indicated no methyl groups present and a KBr disc of the solid was very similar to one of $AlCl_3$.

The reaction was repeated using the same quantities of starting materials and benzene (7 ml.). The tube was heated at 50° for 48 hours and on opening gave 26.44 Nc.c. of methane (infra-red) and 7.34 Nc.c. of trimethylgermane. The non-condensables at -35° contained νGe-H, νGe-CH_3 and νC-H in their infra-red. A similar yellow solid remained which was identified as $AlCl_3$ (infra-red) and contained no methyl groups.

(xii) Triphenylgermane and trimethylaluminium

Triphenylgermane (0.2794 g., 0.0009M) in benzene (5 ml.) was syringed into a sealed tube and trimethylaluminium (0.15 ml., .0014M) added at -196°. The tube was evacuated, sealed and left for 48 hours at 20°. On opening, methane, 2.5 Nc.c. was obtained. Required for dimethyltriphenylgermyl-aluminium is 20.45 Nc.c. The infra-red spectrum of the pumped residue had a ν(Ge-H) at 2020 cm^{-1}.

(xiii) Trimethylstannane and triethylaluminium

Trimethylstannane (0.5364 g., 0.003M) in hexane (5 ml.) was added to a sealed tube and trimethylaluminium (0.4 ml., 0.003M) added at -196°. The tube was evacuated, sealed off and heated at 56° for 12 hours. On opening ethane, 2.37 Nc.c., was obtained. Required for di-ethyl(trimethyl-stannyl)aluminium is 71.71 Nc.c. of ethane. The infra-red of the solution

indicated ν(Sn-H) at 1820 cm^{-1}.

1.3.5 Reactions Involving Anionic Silicon/Germanium Species

(i) Trimethylsilyllithium and dimethylaluminium chloride

This reaction was repeated several times, using slightly varied quantities and "working-up" techniques. The varying products and effects are discussed on p. 33 of this thesis and the following data relate to a typical reaction.

Bistrimethylsilylmercury (5.8765 g., 0.017M) in dry freshly distilled T.H.F. (20 ml.) was slowly added to lithium shot (0.4 g., 0.057M) in T.H.F. (5 ml.) at 0^{o}. The yellow solution turned to a chocolate brown on stirring and warming up. The mixture was refluxed for 12 hours, filtered and the opaque red-brown solution was transferred to a break-seal apparatus, consisting of a bulb and two traps attached to a vacuum line. The solution was cooled to -78^{o}, and dimethylaluminium chloride (3.5 ml., 0.034M) in T.H.F. (5 ml.) was slowly added. The dark colour was discharged immediately, heat was evolved, and the solution turned into an olive-green colour. This was stirred for one hour and then the volume was reduced to about 5 ml. by pumping at 20^{o}.

Tetramethylsilane was identified in these volatiles (v.p.c.).

The distillation bulb "A" was then heated gently to 80^{o} with pumping and the temperatures of the two traps at 0^{o} and -78^{o} respectively. Yellow crystals sublimed from "A" at this temperature into "B" (at 0^{o}) leaving a residual white solid and a pale yellow oily liquid (2 ml.) in A. The pumping was continued for three hours and then the three sections "A" (the bulb) "B" (the trap at 0^{o}) and "C" (the trap at -78^{o}) were sealed off and transferred to the glove box.

A The liquid was separated from the solid (identified as LiCl) by

dissolving in benzene and filtering and pumping down. The infra-red spectrum showed ν(C-H) at 2970 cm^{-1}, ν(Si-CH_3) at 1250 and 1242 cm^{-1} and ν(Si-C) at 833 and 685 cm^{-1}. On exposure to air the oily liquid immediately turned white and semi-solid and the infra-red showed that ν(Si-O) bands at 1069 cm^{-1} and 1008 cm^{-1} had appeared and that the ν(Si-C) bands had decreased in intensity.

A p.m.r. spectrum (benzene as reference) showed broad singlets at 6.30 and 8.73τ (T.H.F.), a multiplet at 9.64τ (Me-Si) and a broad singlet at 10.47τ (Me-Al) integrating in the ratios 1.14:1.14:5.5:1.

Hydrolysis of 0.2014 g., of the liquid produced:

17.95 Nc.c. of CH_4 (5.96 wt. %)

17.06 Nc.c. of Me_3SiH (27.94 wt. %) and T.H.F.

B This consisted of the yellow crystals and a viscous liquid (2 ml.). The yellow crystals decomposed on exposure to air giving mercury. A far infra-red spectrum showed bands at 224.2 cm^{-1}, 315.4 cm^{-1} and 403.2 cm^{-1}.

A p.m.r. spectrum of the liquid showed peaks at 6.44 and 8.70τ (T.H.F.), 9.60 and 9.81τ (Si-CH_3) and 10.27 and 10.44τ (Al-Me) integrating in the ratios of 4.2:1:3.2.

Hydrolysis of 0.2629 g., of the liquid gave:

61.50 Nc.c. of CH_4 (15.7 wt. %)

17.09 Nc.c. of Me_3SiH (21.17 wt. %) and T.H.F.

C A p.m.r. spectrum of this fraction showed mostly T.H.F. with much smaller peaks at 9.59τ (singlet), 9.96τ (multiplet) and 10.95τ (multiplet) integrating: 1:6.5:1.55.

(ii) Trimethylgermyllithium and aluminium trichloride

Trimethylgermylbromide (1.27 ml., 0.01M) was added very slowly to lithium shot (0.14 g., 0.02M) in hexamethyltriphosphoramide (H.M.P.T.,

5 ml.). The blue colour of the solution turned into a golden-yellow as the Me_3GeLi species was generated and heat was evolved. No precipitate was seen. Aluminium trichloride (0.4449 g., 0.003M) in diethyl ether (5 ml.) was slowly added, with stirring, to the solution. The bright golden-yellow colour was discharged immediately and a pale yellow solution with a faint white prepipitate remained. The volatiles at 20° were pumped off and identified as ether. On heating to 140° and with "hard" pumping 1 ml. of liquid distillate was collected while charring occurred in the heated flask. A p.m.r. spectrum of the distillate indicated H.M.P.T. (resonance at 7.60 and 7.84τ) with a very small peak at 10.30τ ($Al-CH_3$). No $Ge-CH_3$ resonance was seen.

Similar results were obtained using triethylgermyllithium in H.M.P.T. and dimethylaluminium chloride.

(iii) Triethylgermyllithium and dimethylaluminium chloride

Bistriethylgermylmercury (3.0007 g., .006M) in benzene (15 ml.) was added to a two-necked flask containing lithium shot (1.3 g., 0.18M) and stirred for 48 hours.

The solution was decanted into a double Schlenk tube and dimethylaluminium chloride (1.3 ml., 0.013M) in benzene (10ml.) added at 0°. A grey precipitate was seen. The solution was stirred for one hour and filtered to give a pale yellow solution.

This was pumped down and yielded a pale green liquid (2.2 g.) A p.m.r. spectrum of this (benzene as reference) showed a multiplet centred at 8.70τ (Ge-Et), a singlet at 9.44τ , a singlet at 10.30τ and a singlet at 10.78τ integrating 31.5:1:1.5:1. The infra-red spectrum showed: ν(C-H) at 2898, 2857 cm^{-1}, δassym(CH_3(Et)) at 1456, 1428 cm^{-1}, δsym(CH_3(Et)) at 1377 cm^{-1}; δsym(CH_2(Et)) at 1258, 1202 cm^{-1} and ν(Ge-C) at 565 cm^{-1}.

A mass spectrum of the involatile fraction showed the liquid to consist of Et_8Ge_3, Et_6Ge_2 and Et_5Ge_2Me.

(iv) Triphenylgermyllithium and dimethylaluminium chloride

Triphenylgermane (3.031 g., 0.001M) in diethyl ether (17 ml.) was syringed into a double Schlenk tube and butyllithium (4.0 ml. of 2.25M hexane solution) slowly added. The solution was stirred for one hour and dimethylaluminium chloride (1 ml., 0.001M) added. Immediately a white precipitate was seen. The solution was stirred for 30 minutes, pumped down and benzene (10 ml.) added. The solution was filtered and on pumping down a white solid (2g.) and a viscous liquid (1 ml.) were obtained. The white solid was chloride free (by analysis) and gave an infra-red spectrum, which included ν(Ge-Ph) at 1073cm^{-1}. A p.m.r. spectrum (in C_6D_6 with T.M.S.) showed Ph-Ge resonances at 2.34 and 2.89τ, Et_2O at 6.56 and 9.32τ and MeAl at 10.1τ, integrating in the ratio 17.5:2.5:1. Hydrolysis of 0.1484 g., of the solid produced 3.70 Nc.c. of methane (1.67 wt. %)

The infra-red spectrum of the liquid was fairly similar to that of Ph_3GeH with ν(Ge-H) at 2032 cm^{-1} and ν(Ge-Ph) at 1086 cm^{-1}. The p.m.r. spectrum (in C_6D_6 with T.M.S.) showed Ge-Ph resonances at 2.35 and 2.92τ, Et_2O resonances at 6.60 and 9.32τ and Me-Al resonances, a singlet at 10.28τ and a quartet at 10.45 integrating 1.25:1.9:1.

(v) Caesium trichlorogermanite and dimethylaluminium chloride

Dimethylaluminium chloride (0.9852 g., 0.0106M) in benzene (10 ml.) was slowly added to caesium trichlorogermanite (3.574 g., 0.0102M) in benzene (20 ml.) in a double Schlenk tube. Some heat was evolved and the slurry was stirred for 12 hours resulting in a pale yellow solution.

The solution was filtered, leaving a white solid (3.48 g.) and a

pale yellow filtrate. A p.m.r. spectrum of this solution (with C_6H_6 as reference) showed a small resoance at 8.55τ, a large broad multiplet centred at 9.01τ and an extremely small resonance at 10.18τ, integrating 6:49:1. The benzene solution was pumped down and yielded a viscous yellow oil (0.4 g.). Both the white solid and the yellow oil were taken into a glove box. An infra-red of the solid showed strong bands at 816 cm^{-1}, 681 cm^{-1} and 657 cm^{-1}. ν(Al-Cl) at 492 and 438 cm^{-1} and ν(Ge-Cl) at 366 cm^{-1}.

The solid contained 35.8% chlorine. The yellow oil gave a very poor infra-red spectrum but micro-cup distillation at $130^{o}/10^{-3}$mm. Hg yielded a colourless liquid (0.05 g.) which gave an infra-red of marked similarity to polymethylgermanes with ν(Ge-C) at 570 and 530 cm^{-1}, δsym(CH_3) at 1230 cm^{-1} and (CH_3) at 820 cm^{-1}. An infra-red spectrum of the flaky residue showed ν(Ge-Cl) at 366 cm^{-1}.

The mass spectrum of the liquid showed among others, $Me_{16}Ge_7$, $Me_{14}Ge_6$ and fragments derived from them, e.g. $Me_7Ge_3^+$ and $Me_5Ge_2^+$. There was a large peak at m/e = 119 assigned to Me_3Ge^+. Another interesting point in the mass spectrum was the presence of a high abundance of chlorinated polymethylgermanes, $Me_2Ge_3Cl_5^+$, $MeGe_3Cl_6^+$ and $MeGe_3Cl_5^+$ being positively identified.

1.3.6 Reactions involving Germyl- and Silylmercury Compounds

(i) Aluminium turnings and bistrimethylgermylmercury

Aluminium turnings (6 g., 0.22M) were stirred under nitrogen in a double Schlenk tube for 12 hours. Bistrimethylgermylmercury (2.5 g., 0.006M) in hexane (15 ml.) was added and the mixture was stirred for 72 hours in the dark. Mercury precipitated out and the pale solution was filtered. The solution was pumped down until there was about 2 ml. of

yellow liquid residue.

A p.m.r. spectrum of this (with C_6H_6 as reference) showed as well as hexane, a multiplet at 9.58τ and a singlet at 10.30τ integrating 7:1. Continued pumping through a -196° trap gave a yellow liquid (1 ml.) with a p.m.r. containing a singlet at 9.59τ and a doublet at 9.51τ. The volatile fraction contained doublets at 9.55, 9.61τ and a singlet at 10.28τ.

An infra-red spectrum of the liquid was very similar to one of polymethylgermanes with ν(C-H) at 2963 cm^{-1}, δasymm(CH_3) at 1424 cm^{-1}, δsym(CH_3) at 1240 cm^{-1} and ν(Ge-C) at 592 and 558 cm^{-1}.

Hydrolysis of 0.1335 g., of the liquid with dilute sulphuric acid yielded no mercury or any volatile gas. The hydrolysis mixture was extracted with diethyl ether and on drying and pumping yielded a liquid which gave a very similar spectrum to the one obtained before .

The v.p.c. of the liquid showed six peaks and by the use of mass spectrometry $Me_{14}Ge_6$, $Me_{12}Ge_5$, $Me_{10}Ge_4$ as well as some $Me_5Ge_3O_3^+$ (probably from cyclic oxides) were unambiguously identified from their parent ions and fragmentation pattern.

(ii) Bistrimethylsilylmercury and di-isobutylaluminium hydride

Bistrimethylgermylmercury (0.5778 g., 0.0016M) in diethyl ether (8 ml.) was syringed into a break-seal apparatus and cooled to -196°. Di-isobutylaluminium hydride (0.4759 g., 0.0033M) was added, the tube evacuated and sealed off. After one week at 20° and 24 hours at 60° there was no colour change or any mercury produced. On opening, no hydrogen, trimethylsilane or isobutane were detected.

(iii) Bistrimethylsilylmercury and dimethylaluminium chloride

Bistrimethylsilylmercury (1.0714 g., 0.003M) in hexane (10 ml.) was syringed into a sealed tube and cooled to -196°. Dimethylaluminium chloride (0.7 ml. 0.007M) was added and the tube was evacuated and sealed. No

reaction was apparent after 48° at 20° and on opening there were no volatiles at -78°.

(iv) Aluminium trichloride and bistrimethylsilylmercury

Aluminium trichloride (1.28 g., 0.009M) was weighed out in a glove box into a small double Schlenk tube. Benzene (5 ml.) was added and a solution of bistrimethylsilylmercury (3.32 g., 0.009M) in benzene (10 ml.) added at 0°. Reaction started immediately and mercury was precipitated out. The solution was stirred overnight, filtered yielding a pale yellow solution. This was transferred to a flask and pumped down yielding a yellow oily residue (~0.6 g.). By comparative v.p.c. the volatiles were shown to contain a molar equivalent of chlorotrimethylsilane. An infra-red spectrum of the yellow oily residue in benzene showed $\nu(Si-CH_3)$, $\nu(Si-C)$ and also $\nu(Al-Cl)$ 435 and 370 cm^{-1}. A large band was noted at 225 cm^{-1}. An equivalent spectra of aluminium trichloride in benzene gave a very weak spectrum and no peak at 225 cm^{-1}.

Hydrolysis of the oily-solid gave no volatiles and reaction of the solid with 1,2-dibromo-ethane (16 hours at 60° in a sealed tube) gave no ethylene or any volatiles, the colour of the solution remaining unchanged. A p.m.r. spectrum (benzene as reference) showed a large multiplet centred at 9.65τ with resonances at 9.51, 9.57, 9.65 and 9.73τ.

1.3.7 Reactions between Trimethyl- and Triethylaluminium with Triphenyl-phosphine-germanium Di-iodide

(i) Trimethylaluminium and triphenylphosphine germanium di-iodide

As a preliminary experiment trimethylaluminium (0.72 g., 0.01M) was slowly added to a solution of triphenylphosphine (2.62 g., 0.01M) in benzene (10 ml.) in a double Schlenk tube. No apparent heat was evolved

and the solution was stirred for one hour, filtered and recrystallised into white plates. These were pumped dry and taken into a glove box (m.p. 66-68°). Hydrolysis of 0.3532 g., yielded 69.8 Nc.c. of methane (13.25 wt. %). Required for Ph_3PAlMe_3 is 13.47 wt. %. Analysis of the white solid gave: C = 75.68% H = 6.97%. Required for Ph_3PAlMe_3 is: C = 75.45% H = 7.18%. The infra-red spectrum of the solid was fairly similar to triphenylphosphine and a p.m.r. spectrum (in cyclohexane) showed two singlets at 2.77τ (P-Ph) and 10.72τ (Al-CH_3) integrating 1.6:1. Required for Ph_3PAlMe_3, 1:1.

Repeating the reaction with similar quantities and stirring for one week and also refluxing for 12 hours yielded the same product.

Germanium di-iodide (9.5 g., 0.0289M) and triphenylphosphine (7.57 g., 0.0289M) were weighed out into a purged three-necked flask, benzene (200 ml.) added and the reaction mixture was refluxed for 12 hours, resulting in an orange solution and a pale yellow precipitate.

Trimethylaluminium (8.5 ml., 0.089M) was added with no immediate evolution of heat. The mixture was stirred for 72 hours at 20° and then 12 hours at 80°.

The orange solution had become paler and a buff-coloured precipitate had appeared. This was filtered off (0.45 g.). No bands were seen in the infra-red and the mass spectrum showed no germanium patterns. Analysis showed: C = 8.63% H = 2.53% P = 12.52% I = 7.98%.

The solution was filtered, hydrolysed very carefully with propane/hexane followed by water and the solution was filtered and dried over anhydrous Na_2SO_4. The solution was then filtered and pumped down yielding a white solid residue (7.13 g.).

An infra-red spectrum of this indicated ν(Ge-C) at 585 and 540 cm^{-1} as well as triphenylphosphine. Separation of the polyalkylgermanes from triphenylphosphine proved difficult but heating the residue in a distillation

apparatus at $110^{o}/10^{-3}$mm. Hg yielded 0.1 g., of a colourless liquid (A). Micro-cup distillation at $110^{o}/10^{-3}$mm. Hg yielded a white sublimate (B) (3.8 g.) and a viscous residue (C).

A An infra-red of the distillate showed a marked similarity to polymethylgermanes and this was confirmed by a low resolution mass spectrum which indicated that the liquid was mainly $Me_{10}Ge_4$ and Me_8Ge_3 with much smaller amounts of $Me_{16}Ge_7$, $Me_{14}Ge_6$ and $Me_{12}Ge_5$.

A p.m.r. spectrum (in benzene) showed broad resonances at 8.50 and 8.91τ and a large multiplet centred at 7.504τ including resonances at 9.41, 9.44, 9.46 9.50 9.52 and 9.56τ.

B The infra-red and mass spectra of the white sublimate showed it to be essentially triphenylphosphine and triphenylphosphine oxide although trace amounts of high molecular weight (m/e > 1000) germanium compounds were present.

C The mass spectrum of this showed the presence of Ph_3P, $Ph_3P = 0$ and substantial amounts of $Me_{10}Ge_7$, $Me_{12}Ge_5$, $Me_{10}Ge_4$ and $Me_5Ge_3O_3^+$ together with smaller amounts of unidentified higher polymers. A large peak was present at m/e = 119 (Me_3Ge^+). No molecular ions corresponding to cyclic organogermanes were seen.

(ii) Triethylaluminium and triphenylphosphine germanium di-iodide

Triphenylphosphine (6.4 g., 0.024M), germanium di-iodide (8 g.,) and benzene (160 ml.) were refluxed for 12 hours. The solution was cooled and triethylaluminium (20 ml., 0.146M) added. Some heat was evolved and the solution was stirred at 20^{o} for 72 hours giving a pale green solution. This was hydrolysed with minimum quantities of propanol and water, filtered, dried over Na_2SO_4 and pumped off leaving a creamy coloured residue (7 g.). An infra-red of the solid showed triphenylphosphine and ν(Ge-C) at 565 and 540 cm^{-1}. Separation of the polymethyl-

germanes from the triphenylphosphine on an alumina column with 60/80 petroleum ether was attempted, but was not successful. Eventually the residue was heated at $120^{o}/10^{-3}$mm. Hg. and 0.5 g., of a colourless liquid was distilled off. The infra-red of this showed: ν(C-H) at 2960, 2940, 2915 and 2880 cm^{-1}; δasymm(CH_3) at 1462 cm^{-1}; δasymm(CH_2) at 1430 cm^{-1}; δsym(CH_3) at 1379 cm^{-1}; δsym(CH_2) at 1215 cm^{-1} a small ν(Ge-O) band at 960 cm^{-1} and ν(Ge-C) at 570 and 530 cm^{-1}.

A p.m.r. spectrum of the distillate in benzene showed a large multiplet centred at 8.83τ.

Three peaks were seen in the v.p.c. (A.P.L. at 200^{o}) and the mass spectrum showed that the liquid consisted of Et_8Ge_3 and Et_6Ge_2 with some $Et_5Ge_2O^{+}$ ion present as well.

A mass spectrum of the residue showed it to consist of mainly triphenylphosphine and triphenylphosphine oxide along with much smaller amounts of $Et_{10}Ge_4$, Et_8Ge_3, $Et_5Ge_3O_3^{+}$ and $Et_7Ge_4O_4^{+}$.

CHAPTER 2

SOME CO-ORDINATION COMPLEXES OF BERYLLIUM

CO-ORDINATION COMPLEXES OF BERYLLIUM

Organoberyllium compounds contain some of the most interesting facets of main group organometallic chemistry. Many of them are electron-deficient polymers or oligomers and the most typical reaction is the relief of electron deficiency by coordination with a donor molecule. The highly polar nature of the beryllium-carbon bond, the electron-deficient bridges to be found in most di-alkyl and di-arylberyllium compounds coupled with the high heat of formation of beryllia make them violently air and moisture sensitive. The beryllia formed on oxidation is an added hazard as it is highly toxic.

It is proposed to briefly discuss the structure, synthesis and some of the general chemical properties of the di-alkyl- and di-aryl-beryllium compounds before examining their coordination chemistry in greater detail.

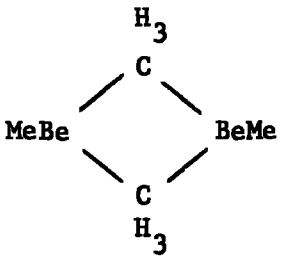
1. STRUCTURE, SYNTHESIS AND SOME GENERAL REACTIONS OF ORGANOBERYLLIUM COMPOUNDS

X-ray analysis[94,95] of solid dimethylberyllium reveals a long chain polymer, the interchain distances excluding an ionic structure. Each beryllium atom is nearly tetrahedrally surrounded by four carbon atoms. Both the beryllium and carbon atoms make use of four tetrahedral (sp^3) atomic orbitals and it is probable[86] that three-centre molecular orbitals $Be(sp^3) + C(sp^3) + Be(sp^3)$ are formed from these. Each of these molecular orbitals would hold two electrons giving a "bent bond"; alternatively each Be-C bond may be regarded as a half bond.

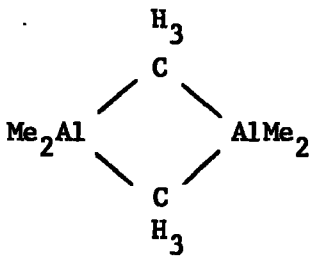
The vapour of dimethylberyllium contains monomeric, dimeric, trimeric and appreciable amounts of oligomeric species and from thermodynamic[96] studies on these, the energy difference between two "half" bonds and one whole bond is 9-12 k cal.mole^{-1} depending on the degree of polymerisation.

The picture of the electron deficient bonding as illustrated by the

previous discussion and (1) may be rather suspect

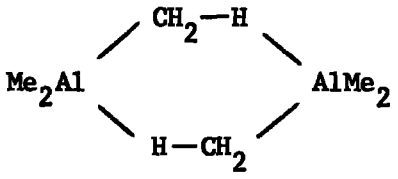


(1)

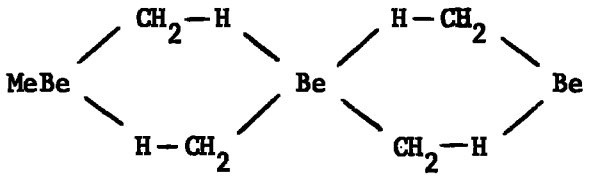


(2)

in view of the newly expressed view[97] of the structure of trimethyl-aluminium dimer. This also was originally formulated as the summetrical methyl-bridged structure (2) having D2h symmetry, based on X-ray structural determination by R.E. Rundle and P.H. Lewis[98], and subsequently confirmed[99,100]. A more refined examination which claimed to reveal the position of the hydrogen atoms has led to the postulate of the hydrogen bridged structure (3).[97] If similar considerations apply to beryllium,



(3)



(4)

then structures such as (4) for the trimer might provide a truer representation of the bonding and molecular geometry. If this is the case it is rather remarkable that the various other spectroscopic studies should not have produced anomalies suggestive of association by hydrogen rather than methyl bridging. (See 3.1.3)

In trimethyl-aluminium the heat of dimerisation is ~ 20 k.cal.mole^{-1}, which is roughly equivalent to the "hydrogen" bonds of 10 k.cal.mole^{-1} each.

Diethylberyllium is dimeric containing two bridging and two terminal

alkyl groups.

Most of the other di-alkyls investigated are dimers with the exception of di-t-butylberyllium, which is monomeric most probably due to steric hindrance of the small beryllium atom by the bulky t-butyl groups.[101]

Diphenylberyllium is a crystalline oligomer with bridging phenyl groups, and because of the greater electronegativity of the phenyl groups, coordinates more strongly than dimethylberyllium to donor solvents.

The analogous aluminium compound is a dimer with co-planar bridging phenyl groups, and the two metal atoms are symmetrically placed above and below this plane.

All of the beryllium di-alkyls and di-aryls can be synthesised using the Grignard reaction with beryllium chloride, beryllium metal with dimethylmercury[103-105] or lithium alkyls with beryllium chloride.[103] The Grignard method has the disadvantage of preparing the di-alkyls in ether, which coordinates, forming etherates. Obtaining the pure di-alkyl, using the Grignard method, is usually effected by slight heating and hard pumping or by a more judicious choice of solvent.

Because of the polarity of the beryllium-carbon bond, beryllium di-alkyls and di-aryls undergo "Grignard" type reactions although generally they appear to be not so reactive as Grignard reagents.

With the exception of dimethyl- and diphenylberyllium, which are stable up to ca. 200°, all of the others are fairly unstable to heat decomposing at temperatures of up to 100° with loss of alkene, alkane and other hydrocarbons usually giving polymeric alkyl-beryllium hydrides.

2. CO-ORDINATION COMPLEXES

(a) Mono-dentate Ligands

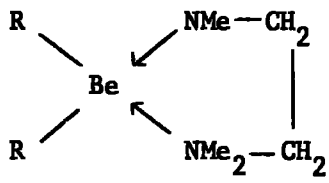
In general only molecules with relatively strong donor properties combine with dimethylberyllium, since the heat of coordination must con-

siderably exceed the heat of polymerisation otherwise the polymeric structure cannot be broken down. Thus trimethylamine forms two complexes with dimethylberyllium, Me_3NBeMe_2[106] (m.p. 36°, v.p. 4 mm. at 36°) and $2Me_3NBeMe_2$[107] (dissociation pressure 22.7 mm. at 0°). Dimethyl- and diethyl-ether also coordinate to dimethylberyllium, although more weakly, and trimethylphosphine causes some interesting phase changes, as its heat of coordination is very nearly the same as the heat of polymerisation and so a variety of complexes are formed.[86] Trimethylarsine and dimethyl-sulphide are not sufficiently strong donors to break down the polymeric structure of dimethylberyllium although dimethylsulphide does form a stable complex[108] with diphenylberyllium in accordance with the greater electro-negativity of the phenyl group. Diphenylberyllium forms much stronger complexes than dimethylberyllium with Me_3N and Et_2O. Pyridine appears to act as a stronger donor than trimethylamine forming a stable bis-complex with both diethyl- and dimethylberyllium and tetramethylhydrazine forms a complex with diethylberyllium[109].

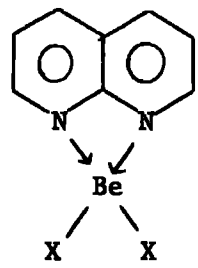
(b) Chelate Complexes

Chelate complexes of di-alkylberyllium compounds are, on the whole, more stable than the corresponding monodentate ones because they maximise the coordination number of beryllium. For example, the chelating di-ether, 1,2,-dimethoxy-ethane forms a crystalline complex which may be sublimed whereas the dimethyl-ether complex has a dissociation pressure of ca. 100 mm. at 20°.

Other chelate complexes are with tetramethylethylenediamine (5) and 2'2'-di-pyridyl (6).[110]



(5)



(6)

The tetramethylethylenediamine series with various R values is interesting because with R = t-butyl, there is steric hindrance at the beryllium atom and proton magnetic resonance studies indicate that only one nitrogen atom at a time is coordinated but with rapid exchange. This exchange slows down below -25° and a distinction is seen in the spectrum[111,112]. The bipyridyl series (6) is also interesting because of the colour, and changes of colour, within the range X = Me, (yellow), X = Cl, (white) and X = Et (red). It has been shown[110] that both λmax. and the extinction coefficients decrease as the electron attracting character of the group X increases. The bipyridyl complexes are also relatively stable to moist air being decomposed only after ∿15 minutes exposure. Other well-characterised chelate complexes are those with tetramethyl-o-phenylenediamine[107] and tetramethyltetrazene[113].

3. CO-ORDINATION COMPLEXES WITH DONORS CONTAINING ACTIVE HYDROGEN

(a) Aminoberyllium Alkyls

Primary and secondary amines form coordination complexes with beryllium di-alkyls, but these readily eliminate alkane[114] unless the hydrogen bound to the nitrogen is sterically prevented from reacting with the carbon atoms of the alkyl groups.

(i) Primary Amines

The reaction between methylamine and dimethylberyllium[114] is typical

of the reactions of primary amines with beryllium di-alkyls, i.e. elimination of alkane (in this case 75%),

$$Me_2Be + H_2NMe \xrightarrow{-90^o} Me_2BeH_2NMe$$

$$Me_2BeH_2NMe \xrightarrow{10^o} CH_4 + (MeBeHNMe)_x$$

$$(MeBeHNMe)_x \longrightarrow [MeBe_2(NMe)HNMe]_y + CH_4$$

leaving a polymeric solid. Similar results have been obtained with t-butylamine and di-t-butylberyllium[115]. The only stable adducts of primary amines with organoberyllium compounds so far isolated have been the aniline and methylamine complexes of diphenylethynylberylliumbis-tetrahydrofuranate[116], $(PhC \equiv C)_2Be(NH_2Me)_2$ and $(PhC \equiv C)_2Be(PhNH_2)_2$.

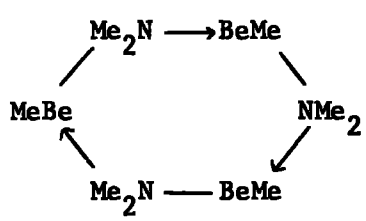
(ii) Secondary Amines

These have been more intensively studied than primary amines. It was shown[114] that dimethylamine forms a complex at 20^o, which loses methane on heating to 44^o to form dimethylaminomethylberyllium trimer.

$$Me_2Be + HNMe_2 \xrightarrow{20^o} Me_2BeHNMe_2$$

$$Me_2BeHNMe_2 \xrightarrow{44^o} \tfrac{1}{3}(MeBeNMe_2)_3$$

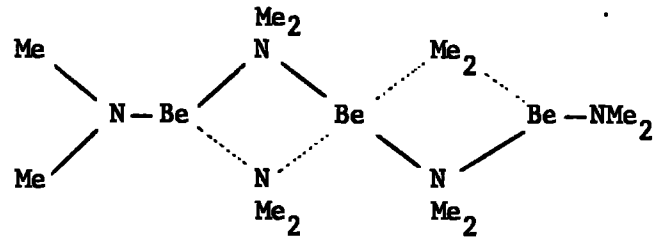
The structure of the trimer is most probably a cyclic six-membered ring with dimethylamino bridges (7).



(7)

Diethyl-[117] and di-isopropyl-beryllium[118] react with dimethylamine below

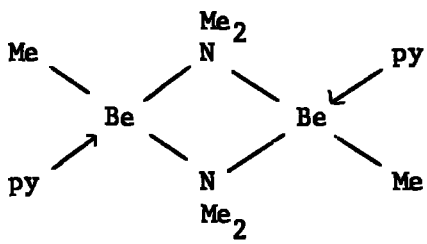
20^{o} to give $RBeNMe_2$ and finally $Be(NMe_2)_2$. The structure of bisdimethylaminoberyllium has been elucidated using p.m.r.[117] and X-ray crystallographic studies[119,120] and is shown in (8).



(8)

There is the possibility of terminal-Be-N-terminal π bonding in this compound as the terminal-Be-N-terminal distance is 1.56Å, the Be-terminal to N-bridging is 1.61Å and Be-centre-N-bridging is 1.76Å. The trend is in the expected direction if π bonding effects are considered.

Many other examples of aminoberyllium alkyls and bis-aminoberyllium compounds are known. They are all dimers or trimers, the degree of association depending most probably on steric and entropy factors. The aminoberyllium compounds, with the beryllium atom three-coordinate, react with some donors forming adducts, thus dimethylaminomethylberyllium trimer reacts with pyridine to form a dimer, (9) and then monomeric $MeBeNMe_2py_2$.[121]



(b) Alkylberyllium Alkoxides

No dialkylberyllium alcoholate complex has been isolated. Alkane evolution takes place rapidly whenever an alcohol is added, giving the alkyl beryllium alkoxide. Most of the alkoxides are tetrameric[112,122],

with structures similar to that of methylzinc methoxide[123], but lower degrees of association occur when the organic groups are large e.g. $(Bu^tBeOBu^t)_2$. The alkoxides can also be synthesised using the reactions between a dialkylberyllium and a ketone or aldehyde[122] or by controlled aerial oxidation[124].

$$Me_2Be + CH_3CHO \longrightarrow MeBe - OCHMe_2$$

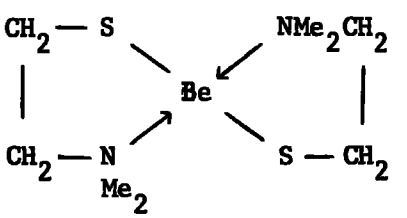
The alkylberyllium alkoxides also give adducts with strong bases. The alkoxides are of structural interest because the presence of two lone pairs and at least two acceptor sites in each monomer, could result in a wide range of associated states. Dimers and trimers would be formed on entropy and valence angle grounds whereas tetramers would give beryllium and oxygen coordination saturation. In fact, as has been said, most alkoxides are tetramers, being dimers only when the organic groups are bulky.

(c) Sulphur Containing Complexes

Dimethylsulphide, 2,5-dithiahexane[108] form complexes with diphenylberyllium and generally the reactions between thiols and most beryllium di-alkyls and di-aryls lead generally to similar products. as with alcohols, if with lesser reactivity, e.g.

$$Me_2Be + 2PhSH \longrightarrow Be(SPh)_2 + 2CH_4$$

The beryllium derivative of 2-dimethylaminoethanethiol is of interest, being monomeric in solution[126](10),



(10)

whereas the analogous alkoxide is oligomeric ($n \simeq 10$).

DISCUSSION

TETRAMETHYLDIARSINE AND DIMETHYLBERYLLIUM

Diethylberyllium reacts with tetramethylhydrazine, Me_4N_2, to form a complex $(Et_2Be)_2Me_4N_2$ [127], compared with the cleavage of the O-O and S-S bonds brought about by reacting Bu^t-O-O-Bu^t with Me_2Be and Et-S-S-Et with Et_2Be giving $[MeBeOBu^t]_4$ and $[EtBeSEt]_4$ respectively. In the reaction with the arsenic analogue, Me_4As_2, and dimethylberyllium, no cleavage or coordination occurred and only starting materials were recovered. Hence the "order of basicities" of the "chelating ligands" R_4X_2 (X = N, O, S, As) is $Me_4N_2 > R_4O_2 \sim R_4S_2 >>> R_4As_2$ and this compliments the series of equivalent monodentate ligands $Me_3N > Me_2O > Me_3P >> Me_2S$, Me_3As in their reactivity to beryllium di-alkyls.

REACTIONS BETWEEN DIMETHYLBERYLLIUM AND TERT-BUTYLAMINE

These reactions can be summarised.

$$Bu^tNH_2 + Me_2BeEt_2O \xrightarrow{\text{below } 20^\circ} \tfrac{1}{3}(Bu^tNHBeMe)_3 + CH_4$$

I

$$\xrightarrow[Bu^tNH_2]{40^\circ} \tfrac{1}{2}[(Bu^tNH)_2Be]_2 + CH_4$$

II

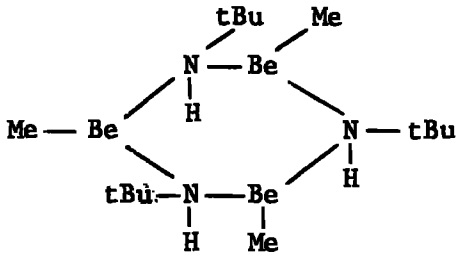
The reaction between equimolar quantities of dimethylberyllium and tert-butylamine went smoothly just below 20° and the tert-butylaminomethylberyllium trimer I was formed. This is an unusual organoberyllium compound in that it is a stable primary amine derivative of an alkylberyllium. The equivalent methylamine compound is a polymer and is much less stable to heat than I, giving 75% of its available methane on heating. The

tert-butylaminomethylberyllium trimer is fairly stable to heat, only 24% of the available methane being formed after 24 hours at 80° and 67% formed after 72 hours at 110°.

$$(Bu^tNHBeMe)_3 \xrightarrow[24\ hrs.]{80^\circ} 24\%\ CH_4$$

$$(Bu^tNHBeMe)_3 \xrightarrow[72\ hrs.]{110^\circ} 67\%\ CH_4$$

From the stability of the compound, the structure of I is probably a six-membered ring, with the tert-butyl groups occupying the equatorial positions, (as in (11)), sterically hindering the hydrogen from reacting with the methyl group attached to the beryllium atom.



(11)

In the p.m.r. of I the methylberyllium protons are at 10.50τ and the t-butyl ones at 8.77τ. No N-H resonance was seen in the p.m.r. (not unusual in a 60 MH_z spectrum) but a weak absorption in the infrared spectrum at 3300 cm^{-1} could be assigned to ν(N-H).

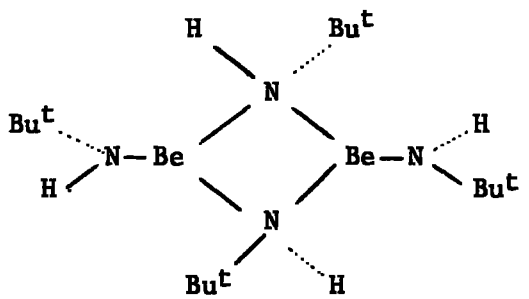
It is interesting to compare the above results with some recent work [128] done on reacting triethylaluminium with tert-butylamine. In this reaction a dimer $[Et_2AlNHtBu]_2$ is formed. The first stage in this reaction is the formation of an adduct $Bu^tNH_2.Et_3Al$ which after 16 hours at 100° formed the crystalline dimer, $(Bu^tNHEt_2Al)_2$ and ethane. This compound on heating to 270° loses another mole of ethane to form the tetramer $[Bu^tNEtAl]_4$. The infrared spectrum of the dimer shows a weak

peak at 3210, possibly due to ν(N-H), and in the p.m.r. spectrum the resonance at 8.83τ is assigned to the tert-butyl group.

The aluminium compound is directly comparable to the beryllium compound, and as it is dimeric, reflects the larger size of the aluminium atom in accommodating the tert-butyl groups around it.

Addition of two moles of tert-butylamine to one of dimethylberyllium etherate resulted in the formation of I, which followed by gentle heating formed bis-tert-butylaminoberyllium dimer (II) with loss of one more mole of methane. II was found to be dimeric in benzene and again the p.m.r. showed no N-H resonance, although the infrared spectrum showed a peak at 3333 cm^{-1} which could be assigned to ν(N-H).

The structure of II is probably as shown in (12).



(12)

existing in the trans form on steric grounds.

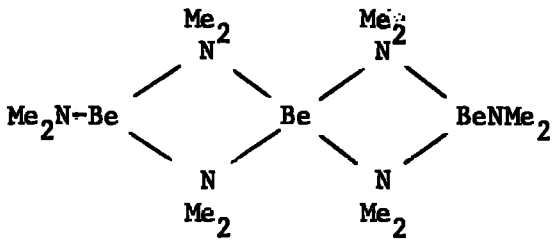
Addition of two moles of dimethylberyllium to one mole of tert-butylamine in an attempt to obtain a cross-linked polymeric structure resulted in only tert-butylaminomethylberyllium trimer being formed and no bis-methylberylliumtertbutylamine polymer.

$$Bu^tNH_2 + 2Me_2Be \xrightarrow[72\ hrs]{50^o} 52\%\ CH_4 + \tfrac{1}{3}(MeBeBu^tNH)_3 + Me_2Be$$

$$No\ \left[(MeBe)_2N\text{-}Bu^t\right]_n$$

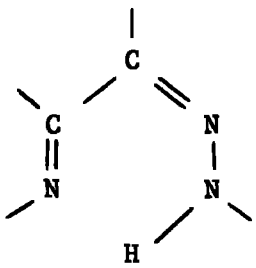
REACTIONS WITH PYRIDINE-2-ALDEHYDEPHENYLHYDRAZONE

In several compounds the beryllium atom appears to bond with some use of its unhydridized p-orbitals. For example, in the compound bis-dimethylaminoberyllium trimer, the structure[117,119,120] is shown in (13).



(13)

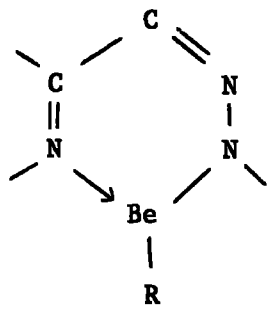
Recent work[119,120] has shown that the terminal-beryllium terminal-nitrogen distance is 1.56Å, the terminal-beryllium central nitrogen distance is 1.61Å and the central beryllium central nitrogen atom is 1.76Å. This trend is in the expected direction if π bonding effects are considered. Also the terminal beryllium atom, the nitrogen atom to which the terminal beryllium atom is coordinated and the carbon atom of the methyl groups on the terminal nitrogen atom are coplanar, and so essentially unhybridised p-orbitals on both the terminal nitrogen and beryllium atoms are then free to form a dative π bond. It was suggested[129] that a system as shown in (14) would be an interesting one.



(14)

If the di-alkylberyllium reacts with the amino-nitrogen, the other nitrogen could then form a dative bond to the beryllium atom and the final system

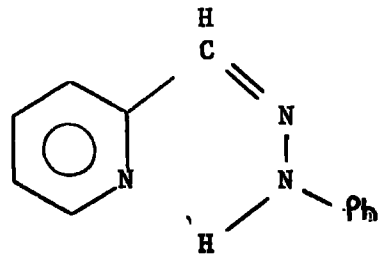
would be as shown in (15).



(15)

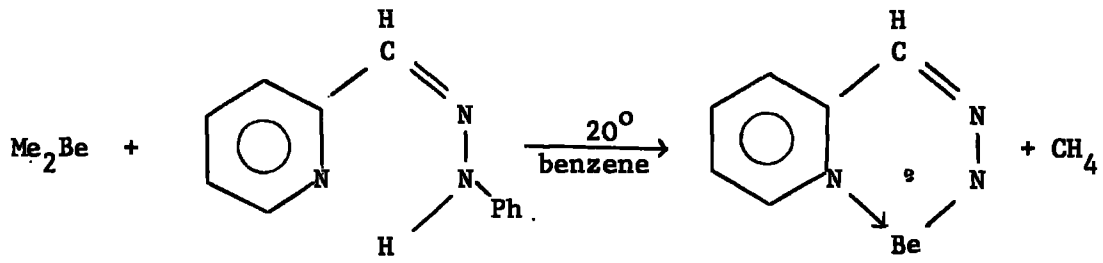
If the ring were planar, delocalisation could arise and a "pseudo aromatic" structure would be formed.

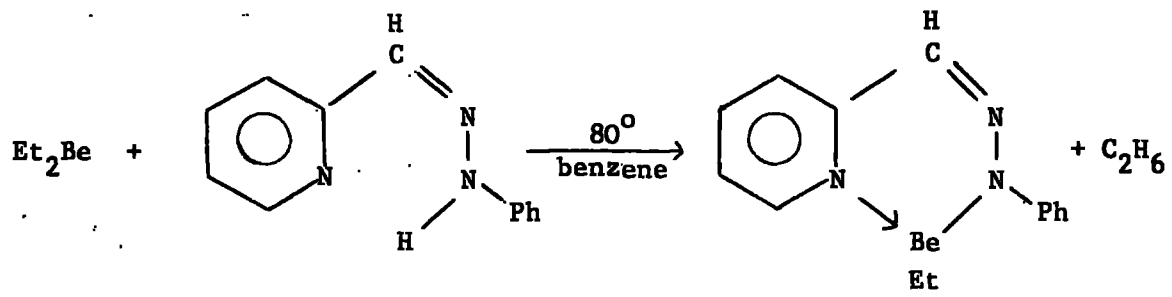
A compound with the required stereochemistry is pyridine-2-aldehyde-phenylhydrazone[130]. (16).



(16)

This compound was eventually synthesised in a pure state and reacted with equimolar quantities of dimethyl- and diethyl-beryllium.





In both cases one mole of alkane was evolved and a yellow precipitate was formed. On recrystallising, the methyl derivative gave beautiful orange-red crystals whilst the ethyl derivative yielded a microcrystalline solid. The methyl derivative was not soluble enough to give an accurate p.m.r. spectrum or molecular weight determination.

The ethyl derivative was monomeric in benzene but its p.m.r. in deuterobenzene, whilst showing C_2H_5Be, C_6H_4N and C-H resonances due to the low solubility and hence weak spectrum sufficiently accurate integration could not be carried out. Both compounds were remarkably stable in the air, tending to last a few hours exposure before turning a brown colour. They were sensitive to sunlight, however, due probably to some degree of nitrogen-nitrogen multiple bonding and were kept in the dark.

The parent compound pyridine-2-aldehydephenylhydrazone was also light sensitive. The specific gravity of the methyl derivative (N_2 glove box) was found to be 1.14 ± 0.05. A preliminary[131] X-ray crystallographic study on the compound shows it to be non-centro-symmetric and at present Dr. Howatson of Wyoming State University is engaged in its structure determination. If the methyl compound is monomeric and if the ring is coplanar, then the compound will contain some very interesting bonding for an organo-beryllium compound.

EXPERIMENTAL

Most of the apparatus and techniques used in preparative organometallic chemistry have been described elsewhere in this thesis. The following section contains the parts relevant to the investigation of organoberyllium compounds.

GENERAL HANDLING

As all beryllium compounds are toxic, the utmost care was taken in disposing of residues. This was usually done by soaking all apparatus used in 2N.sulphuric acid prior to general cleaning.

ANALYSES

1. Gas analyses

A weighed amount of the sample was attached to the vacuum system. The sample was cooled to -196° and degassed. 2-Methoxyethanol was then run onto the sample. The mixture was allowed to warm up slowly and the hydrolysis was completed by the addition of 2N.sulphuric acid. If the compound contained a volatile amine, the sample was pumped hard before addition of H_2SO_4, because any amine present would interfere with the end-point in the subsequent volumetric determination of beryllium. The gases were identified by their infrared spectra. All gas volumes are corrected to N.T.P. and are referred to as N.c.c.

2. Beryllium analyses

The solution was made up to a standard volume containing approximately 6 mg. Be/100 ml. Aliquots of 20 ml. were treated as follows:
5 ml of 0.5M sodium potassium tartrate were added and then two drops of 0.1% alcoholic solution of bromothymol blue. The solution was then made alkaline by addition of 0.5N sodium hydroxide until a blue colour persisted. The solution was then made neutral (green) by the addition of 0.1N sulphuric acid.

The tartrate was added to complex the beryllium and avoid the precipitation of $Be(OH)_2$. The complex was then destroyed by adding 5 ml. of M.potassium fluoride solution which liberated the hydroxide ion,

$$\text{complexed } \left[Be(OH)_2\right] + 4F \longrightarrow BeF_4^{2-} + 2OH^-$$

and caused the solution to become alkaline (blue). After two minutes the solution was titrated with 0.1N. sulphuric acid back to the green end-point previously obtained. The reaction is non-stoichiometric and requires calibration with standard beryllium solutions each time new solutions are prepared. The presence of bases or a large concentration of ions is not desirable due to drifting of the end-point.

It was found that the above method when applied to the pyridine-2-aldehydephenylhydrazone compounds did not give reproducible results, probably due to strong complex formation with the beryllium ion. Various methods were tried to overcome this including precipitation, extraction with NaOH and benzene, and oxygen flask experiments. The optimum method for these type of compounds was found to be to use a pyrolysis technique. About 5 g. of small pumice pieces were heated to constant weight in a porcelain crucible. About 0.2 g. of the beryllium compound was added to the pumice, a few drops of conc. HNO_3 added and the crucible was then heated to constant weight. The residual weight was beryllia adsorbed on the pumice and of course was carefully disposed of.

3. Amine analysis

The acid solution from hydrolysis was made alkaline with strong NaOH solution and the amine steam-distilled into excess standard acid. The excess acid was then titrated with standard alkali.

MOLECULAR WEIGHTS

Molecular weights were determined cryoscopically in benzene solution where solubility permitted. The cryoscopic constant of the benzene used

was determined by calibration using freshly sublimed biphenyl. All molecular weight determination were carried out under a static atmosphere.

PREPARATION AND PURIFICATION OF STARTING MATERIALS

TERT-BUTYLAMINE

This was distilled (b.p. 45.2°/760 mm) from CaH_2.

TETRAMETHYLDIARSINE

This was available in a pure state in the laboratory. [Courtesy of Mr. R. Coult, University of Durham].

BERYLLIUM CHLORIDE (see Fig. 1)

This was prepared in 95% yield by burning beryllium powder (T = 400°) in a chlorine atmosphere with nitrogen as diluent. It was normally done on a 0.5M scale. The precautions taken were to ensure that the constriction was kept clear of the sublimed beryllium chloride and also to avoid localised heating as silicates are formed.

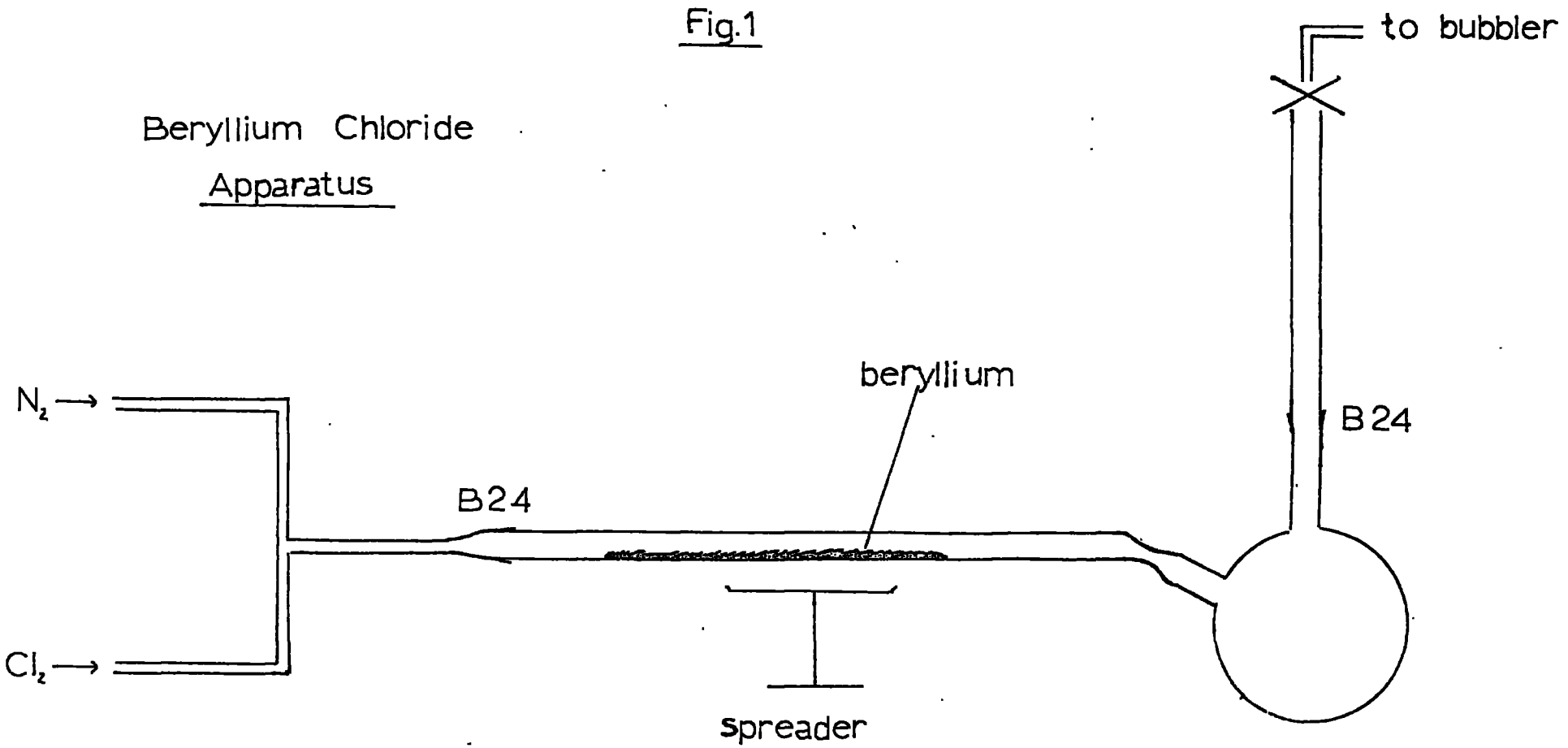
BERYLLIUM DIALKYLS

Preparations were usually carried out on a 0.5M scale. Beryllium chloride was cooled to -78° and diethyl ether slowly added. The solution was allowed to warm to room temperature and was stirred until all of the beryllium chloride had dissolved. The required amount of Grignard reagent was added over a period of an hour with vigorous stirring. Magnesium halides were precipitated at once and the reaction mixture became warm. After completion of the addition of the Grignard, the mixture was stirred and then allowed to settle. Then the ethereal solution was decanted and the volume reduced to 150-200 ml. by distillation. Dimethylberyllium etherate was concentrated using the apparatus devised by Gilman and Schulze[102] while diethylberyllium etherate was distilled at 70° and 1 mm. Hg pressure. Yields of 80-85% were obtained

Fig.1

Beryllium Chloride

Apparatus



and losses can be accounted for in the numerous transference reactions.

PYRIDINE-2-ALDEHYDEPHENYLHYDRAZONE

It was found that the literature preparation of this compound was unsuitable for the intended reactions because of the use of protic solvents in its synthesis and the presence of chloride ion in the final compound.[130] Eventually the phenylhydrazone was obtained pure by direct addition of pure pyridine-2-aldehyde to a solution of phenylhydrazine in benzene, heating at 78° for twenty minutes and recrystallising twice from benzene. The infrared spectrum of this compound was virtually identical to the compound as prepared in the literature, but its melting point was slightly higher, 176-177° as against the literature 173-176°. The pure compound was kept under nitrogen in the dark as it had a tendency to decompose after a few days in the sunlight. The decomposition is probably due to the -C=N-N- linkage in the compound being destroyed by the u/v radiation in sunlight.

DIMETHYLBERYLLIUM ETHERATE WITH TETRAMETHYLDIARSINE

Tetramethyldiarsine (1.45 ml. 0.010 M.) in 10 ml. of diethyl ether was added slowly to 6.94 ml. of 1.445 M. dimethylberyllium etherate solution, 0.010 M, at -196° in a double Schlenk tube. The reaction mixture was allowed to warm up slowly and it remained colourless. No effervescence was seen. The solution was pumped down and tetramethyldiarsine was identified in the cold trap. A white solid remained which was insoluble in benzene, hexane and toluene and analyzed to dimethylberyllium. The reaction was repeated in benzene with, at 80°, similar results.

DIMETHYLBERYLLIUM ETHERATE WITH TERT-BUTYLAMINE

1. EQUIMOLAR. FORMATION OF THE METHYL TERTBUTYLAMINOBERYLLIUM TRIMER

Freshly distilled tert-butylamine (1.05 ml. 0.010 M.) in 10 ml. of diethyl ether was added to 6.94 ml. of 1.445 M. dimethylberyllium etherate solution, 0.01 M. at -196°, in a double Schlenk tube. The system was

evacuated and the reaction mixture allowed to warm up slowly, with stirring, to room temperature. The reaction proceeded just below room temperature and was quite vigorous. Effervescence was seen. The gases evolving were fractionated through a -196° trap and 210 N.c.c. of pure methane were evolved (224 N.c.c. of gas would be formed if one methyl group on Me_2Be was replaced).

The solution was pumped down and a white solid residue remained. This was very soluble in hexane, pentane and benzene and was finally recrystallised from pentane at -78° as small colourless prisms m.p. 75° dec.

Analysis

Hydrolysable methyl. Found: 15.29%. Calc. for $(MeBeNHBu^t)_3$: 15.60%.

Beryllium. Found: 9.41%. Calc. for $(MeBeNHBu^t)_3$: 9.16%.

M.Wt (cryoscopic in C_6H_6). Found: 278, 249. Calc. for trimer $(MeBeNHBu^t)_3$: 288.

^1H n.m.r. in C_6H_6 (TMS): CH_3-Be, τ, 10.50; $(CH_3)_3$-C, τ, 8.77.

Areas Me_3C, MeBe: 3 : 1. No visible N-H.

I.R. in Nujol mulls. w = weak, s = strong, m = medium, sh. = shoulder, br. = broad.

3300w; 3257w; 1576m; 1351s; 1274m; 1258m; 1188s; 1172w; 1152m; 1136; 1026sh.; 1015m; 971m; 952sh.; 917w; 905w; 862s; 823 s.br.; 794s.br.; 735m.

2. ACTION OF HEAT ON THE METHYLTERTBUTYLAMINOBERYLLIUM TRIMER

Methyltertbutylaminoberyllium (0.0914g.) was weighed out in a glove box and dissolved in 10 ml. of toluene. This was syringed into a sealed tube apparatus, cooled to -196°, evacuated and the constriction sealed. The solution was heated at 80° for 24 hours, frozen down and the tube opened. 5.20 N.c.c. of methane were evolved. 100% reaction requires 21.32 N.c.c. The experiment was repeated using 0.1546 g. 0.0016 M. of the compound and the solution was heated for 72 hours at 110°. 23.5 N.c.c. methane obtained

100% reaction requires 35.1 N.c.c. The solution had also turned a light brown colour.

3. DIMETHYLBERYLLIUM ETHERATE AND TERT-BUTYLAMINE IN A ONE : TWO MOLAR RATIO. FORMATION OF BIS-TERTBUTYLAMINOBERYLLIUM DIMER

Dimethylberyllium etherate, 0.694 ml. of 1.445 M. solution (0.001M.) was syringed into one limb of a double Schlenk tube and 0.25 ml. (0.0025M.) of tert-butylamine was syringed into the other limb. The system was frozen down to -196° and evacuated and then the tert-butylamine was distilled onto the dimethylberyllium etherate. The vessel was allowed to warm up and reaction took place. The system was heated at 40° for three hours and 44.57 N.c.c. of pure methane obtained, (for both methyl groups replaced 44.82 N.c.c.). The ether was pumped off and a white residue was left. The compound was soluble in pentane, hexane, and benzene. It was recrystallised from pentane as white crystals at -78°, m.p. 96-97° with discolouration.

Analysis

Hydrolysable methyl. Found: 0%. Calc. for $C_6H_{20}N_2Be$: 0%.

Beryllium. Found: 5.82%. Calc. for $C_6H_{20}N_2Be$: 5.88%.

Amine. Found: 93.76%. Calc. for $C_6H_{20}N_2Be$: 94.12%.

^1H n.m.r. in benzene: C-CH_3, 8.68τ, 8.80τ, 7:1. No N-H peaks.

Molecular weight in benzene. Found: 319,280. Calc. for $(C_6H_{20}N_2Be)_2$: 306.

I.R. Nujol mull. 3333w; 1408m; 1355s; 1258sh; 1235br.s; 1205br.s; 1181s; 1170sh; 1121s; 1022s; 949s; 917m; 913sh; 847s; 826-803s.br; 763s; 741s; 750s; 629m.br; 567m.br; 513-497m.br.

4. DIMETHYLBERYLLIUM ETHERATE AND TERT-BUTYLAMINE IN A TWO TO ONE MOLAR RATIO. ATTEMPTED FORMATION OF BIS-METHYLBERYLLIUMTERT-BUTYLAMINE POLYMER

Dimethylberyllium etherate, 1.388 ml. of 1.445M. solution (0.002M.) was syringed into a sealed tube apparatus. 22.41 N.c.c. of pure, dry

tert-butylamine was measured by a Töpler pump and condensed onto the dimethylberyllium etherate. The constriction was sealed and the tube was heated at 50° for 72 hours and then broken open and the gas measured. Expected for complete reaction of amino-hydrogens: 41.06 N.c.c. methane, Found: 21.35 N.c.c. methane (52%).

5. DIMETHYLBERYLLIUM ETHERATE AND PYRIDINE-2-ALDEHYDEPHENYLHYDRAZONE

In an initial experiment, 0.1975 g. (0.001M.) of pure pyridine-2-aldehydephenylhydrazone was added to a 2N. flask attached to a vacuum line. 10 ml. of toluene was added, the solution was degassed and let down to nitrogen. 0.600 ml. (0.001M.) of dimethylberyllium etherate was syringed in and the system was frozen down to -196° and evacuated. It was then allowed to warm up. Reaction occurred at the rate of dissolution of the pyridine compound and took place well below room temperature. When the effervescence had finished the amount of methane formed was measured. Found: 22.07 N.c.c. For one methyl group replaced 22.46 N.c.c. would be formed. On a preparative scale 1.96 g. (0.010M.) of pyridine-2-aldehydephenylhydrazone was added to a large Schlenk and 60 ml. of toluene was added. Dimethylberyllium etherate 5.80 ml. of 1.72 M. solution (0.01M.) was added at -196°. The reaction mixture was allowed to warm up and the initial yellow colour deepened, effervescence was seen and the colour turned eventually to crimson. The solution with some precipitate was filtered and recrystallised by adding hexane. Optimum recrystallisations giving large orange-red prisms were performed using benzene-toluene mixtures. The orange-red crystals decomposed above 140°, were not soluble enough in deuterobenzene for a good p.m.r. spectrum, soluble enough in benzene for a molecular weight determination or volatile enough for a mass spectrum. They were fairly sensitive to light turning a brown-yellow colour after about 24 hours exposure but were not violently reactive to air or water.

Analysis

Hydrolysable methyl. Found: 6.74%. Calc. for $C_{13}H_{13}N_3Be$: 6.80%.

Beryllium. Found: 4.16%. Calc. for $C_{13}H_{13}N_3Be$: 4.09.

Specific gravity is 1.14 ± 0.05.

I.R. Nujol mull. 1607m; 1587sh; 1562sh; 1493m; 1351m; 1307w; 1274w; 1252sh; 1217m; 1147m; 1170sh; 1109w; 1066w; 1050w; 1026w; 999w; 962m.br; 879m; 813m.br; 778m.br; 757m.br; 746m.br; 723m.br; 697m; 680sh; 673m; 540w.br; 513w.br;

6. DIETHYLBERYLLIUM ETHERATE AND PYRIDINE-2-ALDEHYDEPHENYLHYDRAZONE

Pyridine-2-aldehydephenylhydrazone, 1.97g. (0.01M.) dissolved in 80 ml. of a toluene/benzene mixture (50%) was added to a large Schlenk tube. Diethylberyllium etherate 6.89 ml. of 1.45M. solution (0.01M.) was added at -196°. On warming the orange colour turned to crimson and slight effervescence was seen. The reaction mixture was warmed up to 80° and left for an hour, filtered and attempted to crystallise. This was difficult as on pumping, the red crystals formed, yielded a yellow brown solid. Eventually from a toluene/cyclohexane mixture, a fine yellow microcrystalline compound was obtained.

Analysis

Hydrolysable ethyl. Found: 12.71%. Calc. for $C_{14}H_{15}N_3Be$: 12.39%.

Beryllium. Found: 4.16%. Calc. for $C_{14}H_{15}N_3Be$: 4.09%.

Molecular weight (cryoscopically in C_6H_6): Found: 241, 247.

Calc. for $C_{14}H_{15}N_3Be$ monomer: 234.

I.R. Nujol mull. 1739w; 1610m; 1592sh; 1493m; 1439m; 1377m; 1355m; 1302w; 1258m; 1235sh; 1218m; 1149m; 1026w.br; 984w; 935w; 877w; 800m.br; 808sh; 747m; 713m; 694w; 631w.

The p.m.r. spectrum was run in deuterobenzene with TMS but was quite complicated. Due to lack of accurate integration the various peaks could not

be accurately assigned but were as follows:

multiplet at 2.86τ (C_6H_5), multiplet at 3.86τ (C_6H_4), quartet at 6.80τ, triplet at 8.77τ and a singlet at 8.43.

CHAPTER 3

MASS SPECTROSCOPIC STUDIES ON THE GROUP III METAL ALKYLS

MASS SPECTROSCOPIC STUDIES ON THE GROUP III METAL ALKYLS

3.1 Introduction

The purpose of this work was to examine the high resolution mass spectra of trimethylboron, trimethylgallium, trimethylindium and trimethylthallium at low sample and source temperatures, in order to discover and investigate any associated species, to tabulate the ions and to discover the variation of ion abundances with source temperature and ionising voltage. Trialkylaluminium and di-alkylberyllium compounds have already been investigated in this manner[132-135].

It is proposed to discuss briefly the trends within the group, the structure and some relevant chemistry of the group III metal alkyls and then to generally survey the mass spectroscopic studies on main group organometallic compounds.

3.1.1 Trends Within the Group

The electronic structures and some relevant physical data of the elements are shown in Fig. I(a) and physical data on the trimethyl derivatives are shown in Fig. I(b).

The general trend within the group is clearly from non-metallic to metallic in character. This is manifested by the general lowering of the first ionisation potential, the larger atomic radii, the lowering of the electronegativity and the weakening of the mean element-carbon bond strength.

Another trend is seen in the increasing stability of the univalent state as the group is descended. While this is unimportant in boron and aluminium at ordinary temperatures, in thallium the Tl^{I} - Tl^{III} relationship is a dominant feature of the chemistry. The stability of the univalent state in thallium chemistry is attributed to the presence of the two 6s electrons - the so-called "inert pair". Whilst this is a useful

Figure 1(a)

Element	Electronic Structure	1st I.P.	Electronegativity*	Atomic Radius Å
B	He $2s^2sp$	8.30	2.01	0.88
Al	Ne $3s^23p$	5.98	1.47	1.26
Ga	Ar $3d^{10}4s^24p$	6.00	1.82	1.33
In	Kr $4d^{10}5s^25p$	5.79	1.49	1.66
Tl	Xe $4f^{14}5d^{10}6s^26p$	6.11	1.44	-

*Allred-Rochow

Figure 1(b)

Compound	m.p.	b.p.	ΔHM-C* kcal.mole^{-1}	Trouton Constant
Me_3B	-153°[136]	-21.8°[136]	84.4[137]	22.8[136]
Me_3Al	15°[136]	126°[136]	70.0**[86]	24.7[136]
Me_3Ga	-15.7°[139]	56°[139]	59.5[138,140]	22.5[141]
Me_3In	88.0°	136°[86]	47.2[142]	-
Me_3Tl	38.5°	147°(extrap)[86]	27.4[142]	-

*mean M-C bond strength

**for monomer

label, the true cause of this phenomenon is most probably the decreasing strengths of bonds as the group is descended[20].

The discontinuity of the electronegativities can also be attributed to the electronic structures of the elements. These values reflect the filling of the "d" and "f" shells in the transition elements and lanthanides which affects the screening of the valence electrons in the elements following them. The physical properties of the trimethyl derivatives (see Fig. I(b)) also reflect the increasing metallic character as the group is descended. Anomalies such as the high boiling point of Me_3Al and the high melting point of Me_3In can be explained by the associated nature of these compounds.

3.1.2 Me_3B Structure and some Chemical Properties

Trimethylboron was first synthesised by Frankland in 1862[143] from dimethylzinc and boron trichloride.

Other syntheses of the trialkylboron compounds include the reactions of boron trifluoride etherate with Grignard reagents and tributylborate with trialkyl-aluminium compounds[144].

Trimethylboron is spontaneously inflammable but is unaffected by water under ordinary conditions. The structure of the molecule has been determined[145] and it is monomeric and trigonal in shape. The monomeric nature of the compound has been confirmed by Raman[146], infra-red[147,148] and ^{11}B nuclear magnetic resonance studies[149], although low temperature proton magnetic resonance on the liquid has not yet been attempted.

The monomeric nature of trimethylboron has been attributed[150-152] to exceptionally strong trigonal hyperconjugation in which there is a drift of electron density to the B-p^{π} orbital from the pseudo p^{π} orbitals which can be formed from the hydrogen atoms on the methyl groups[143]. This would lower the energy of the molecule, not only by delocalisation but also by partial neutralisation of the change separation in the σ bonds. The

exceptionally strong hyperconjugation in Me_3B tends to reduce the ability of the molecule as a Lewis acid towards Me_3N. The order of Lewis acidity decreases in the sequence $Me_3Al > Me_3Ga > Me_3In > Me_3B > Me_3Tl$ [153].

In the reactions between Me_3N, $(CH_3)_3B$ and $(CD_3)_3B$, (1) and (2)

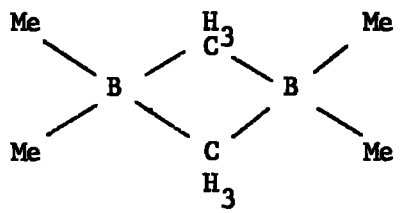
$$(CH_3)_3B_{(g)} + Me_3N_{(g)} \longrightarrow Me_3N\text{-}B(CH_3)_{3(g)} \qquad (1)$$

$$(CD_3)_3B_{(g)} + Me_3N_{(g)} \longrightarrow Me_3N\text{-}B(CD_3)_{3(g)} \qquad (2)$$

the equilibrium constant of (2) is greater than (1)[164], which is in agreement with the expectation that replacement of hydrogen atoms leads to a reduction in hyperconjugation with resultant increase in Lewis acidity.

Other evidence for hyperconjugation includes the observation that in a B - C = C system the $\nu(C = C)$ shifts to a lower wave number, implying that the B - C bond has an order >1.

Although hyperconjugation does seem to explain the reason for the non-association of trimethylboron other factors could also play a part. The boron-carbon bond length in Me_3B is 1.56Å and the C - $\hat{B}$ - C is 120 $\pm$ 3° . For the hypothetical dimer (3), the two boron atoms would be extremely close together and inner-shell repulsion forces would make (3) unstable.



(3)

The chemistry of trimethylboron and other alkylboranes has been extensively reviewed[86,148,155]. Typical reactions of trimethylboron include the formation of stable adducts with Lewis bases (even those containing amino hydrogen atoms) and formation of dialkylboron halides and alkane

when reacted with hydrogen halides.

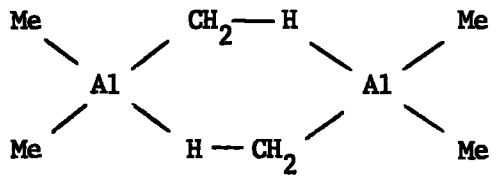
3.1.3 Me_3Al Structure and some Chemical Properties

Trimethyl-aluminium was first symthesised in 1865[156] by G.B. Buckton and W. Olding from aluminium and dimethylmercury. Within the last twenty years industrial interest in trimethylaluminium and other alkyaluminium compounds has accelerated to such an extent that most of the common alkyls are available commercially. This recent growth is mostly due to K. Ziegler and G. Natta who developed them for use as catalysts in isotatic polymerisation[157,158]. With very few exceptions the aluminium alkyls and their derivatives are highly air and moisture sensitive and most of them are spontaneously inflammable.

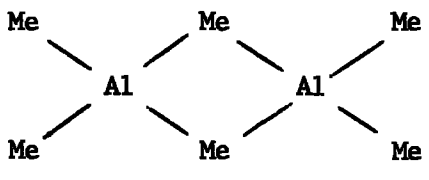
Trimethylaluminium is dimeric in benzene solution[159] and a monomer-dimer equilibrium has been observed in the vapour from 100° to 160°, the heat of dissociation to two moles of monomer being 20.4 kcal.mole^{-1}.[160] Tri-ethyl-, tri-n-propyl- and tri-n-butylaluminium are also dimeric in benzene and p.xylene and a recent study[161] using p.m.r. has shown that tri-isobutyl aluminium is 39.4% associated at 10°, the heat of dissociation being 8.1 kcal.mole^{-1}.

The bridge structure of trimethylaluminium was first indicated by its Raman[162] and infra-red spectra[163], and was confirmed by X-ray crystal analysis[98,99]. The structure of the monomer has been studied by electron diffraction methods and is a planar trigonal shape[164].

There has been a little controversy recently following the paper by S.C. Nyburg et.al.[97] which claimed to locate the position of the hydrogen atoms within the molecule and proposed the structure (4) (see pp. 63,64 of this thesis).



(4)



(5)

An even more recent study[165] using ^{27}Al nuclear quadrupole resonance techniques has confirmed the structure (5). The latter study indicates that the high asymmetry parameter found for Al_2Me_6 at -77° would seem to rule out (4) since in (4) the Al-C bonds would all be similar and the asymmetry parameter consequently small. The structure (5) on the other hand would be like aluminium tribromide dimer for which a very similar asymmetry parameter has been reported[166].

It is felt that owing to the preponderance of spectral data supporting the Lewis-Rundle structure (5), and the inherent difficulty in locating individual hydrogen atoms by X-ray diffraction, that the two-electron hydrogen bridge structure (4) is probably wrong.

The actual structure of the trimethylaluminium dimer is thus akin to the structure of the dimethylberyllium polymer already described in this thesis (pp.62-3). The rather small Al - C - Al angle 70° is required for good overlap between the Al sp^3 and C sp^3 orbitals and the reason for the dimerisation of trimethylaluminium is primarily the high tendency of aluminium to make use of all four of its available low energy atomic orbitals. The Al - C - Al bridge bonds are regarded essentially as formed by "bent" three-centre molecular orbitals (Al sp^3 + C sp^3 + Al sp^3). There would be two such orbitals, each occupied by a pair of electrons so each Al - C bridge bond could be regarded as a half bond. A point of interest is that the Al - Al internuclear distance 2.55Å, is only slightly greater than twice the Al single bond covalent radius (1.26Å) and this implies that

there could be some Al - Al bonding. On this last point a recently described compound[167], formed from Me_6Al_2 and $B_2[NMe_2]_4$, is formulated as $Al_3Me_3(NMe_2)_2$ in which Al - Al covalent bonds are present.

Proton[100,168] and ^{27}Al[169] nuclear magnetic resonance studies have been done on trimethylaluminium, and other p.m.r. studies on mixed alkyl and aryl compounds[170-172]. The p.m.r. spectrum of trimethylaluminium at 20° shows a single resonance due to rapid exchange between bridging and terminal methyl groups. This exchange is slowed down with decreasing temperature until at -78° both the bridging and the terminal methyl group resonances are seen[100].

The chemical reactions of trimethylaluminium and other trialkyl compounds have been the subject of a large number of publications[86,157,158] and are summarised below.

(a) The formation of co-ordination complexes with Lewis bases: e.g. $R_3Al\ NMe_3$. In these reactions the main points are that the heat of association of the ligand must be able to break the methyl bridges and that the aluminium atom tends to favour a co-ordination saturation of four.

(b) The formation of co-ordination complexes with ligands containing acidic hydrogen: e.g. $(Me_2AlOMe)_3$. These complexes are usually dimers or trimers, which one being formed probably decided on entropy factors, favouring dimers or steric factors generally favouring trimers[86].

(c) The formation of anionic co-ordination complexes with group I alkyls: e.g. $Li[AlMe_4]$. These are of interest because they have interesting structural features such as electron-deficient bonding, and in the case of $K^+[Al_2Et_6F]^-$, "fluorine" bonding. In the latter compound, the anion consists of two Et_3Al moeties separated by a fluorine atom, the Al - F - Al angle being 180°[173]. The chemistry of these compounds has been comprehensively reviewed by R. Köster and P. Binger[158].

(d) The thermal decomposition of aluminium alkyls is discussed in section 3.3.4.

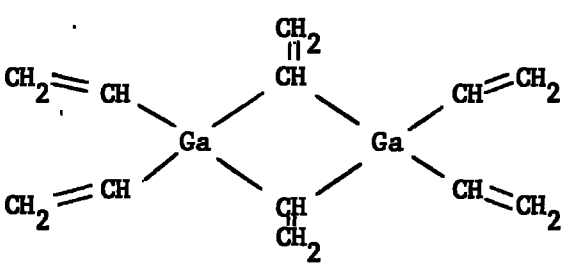
(e) The reactions of trialkylaluminium compounds with alkenes and alkynes and as alkylating agents has been discussed by H. Zeiss[157], R. Köster and P. Binger[158] and H. Reinheckel et.al.[174].

3.1.4 Me_3Ga Structure and some Chemical Properties

Trimethylgallium was first synthesised in 1933 by C. Kraus and F.E. Toonder from dimethyl zinc and gallium trichloride[175]. An alternative method is to reflux dimethylmercury with gallium metal and with a trace of methylmercuric chloride as catalyst[139,176].

Dispite some earlier reports[141,177] of associated species present in trimethyl- and triethyl-gallium, Raman[178] and infra-red spectra[179-180] of the liquid and vapour show that these compounds exist essentially in the monomeric form. No X-ray or electron diffraction studies on the trimethyl derivative have yet been attempted although an extensive study[181] using proton magnetic resonance techniques has confirmed the monomeric nature of Me_3Ga and Et_3Ga. The methyl protons in Me_3Ga resonate at 9.97τ in cyclopentane. This alters by only 0.03 p.p.m. upfield relative to cyclopentane on cooling to -100° and by only 0.01 p.p.m. upfield on increasing the concentration fourteen times.

However, tri-vinylgallium[182], from Me_2Hg and gallium is dimeric in benzene with the proposed structure (6).



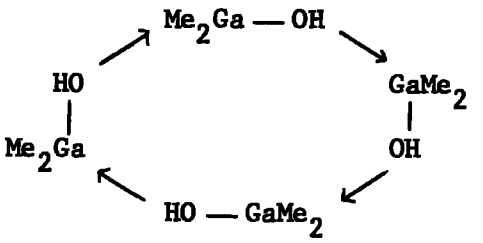
(6)

Other vinyl or ethynyl type gallium alkyls which have since been made are dimethyl(phenylethynyl)gallium[183], tripropenylgallium[184] and dimethylvinylgallium[185]. These are all dimers in benzene solution, but proton magnetic resonance studies indicate that with the compound in a non-polar solvent, there is rapid exchange between bridging and terminal groups, even at temperatures as low as -50^{o}_{j} and only one type of signal is seen. However when a donor solvent is added there is a change of shift which indirectly supports the proposed structures. The coupling constants of $Me_2GaCH = CH_2$ have been examined[185] and show only a very small dependence on temperature and concentration. This implies that the electronic structure of the vinyl group has not undergone a major disruption. The changes in chemical shift are consistent with the formation of a bridge bond through the sp^2 orbital of the vinyl group. The enhanced stability of vinyl-type bridges over saturated systems is most probably due to the fact that the non-bonding atomic orbital on the metal has the appropriate symmetry to interact with the π orbitals of the vinyl groups and so stabilise the system. Presumably the bridging carbon atoms have approximately tetrahedral coordination.

Trialkyl-gallium compounds are spontaneously inflammable and hydrolysed by water. However the alkyls of gallium differ from those of aluminium in that while the first alkyl group is removed readily the remaining two are much more difficult. Reaction between trimethyl-gallium etherate and water gives the crystalline $(Me_2GaOH)_4$[186].

$$4Me_3GaOEt_2 + 4H_2O \longrightarrow 4(Me_2GaOH)_4 + 4Et_2O + 4CH_4$$

This compound has been examined by X-ray diffraction[187] and is a tetramer with an eight membered ring (7).



(7)

The reactions of trialkylgallium compounds with electron donor molecules reflect the lower Lewis acidity of them compared to trialkylaluminium compounds. For example, the ether complex is appreciably dissociated[175] in the vapour phase. However, occasionally, weak donors which do coordinate to trimethylgallium do not react with trimethylaluminium, because of the 20.4 kcal.mole^{-1} energy required to break the methyl bridges, e.g. $AsMe_3$ co-ordinates to Me_3Ga but not to Me_3Al.

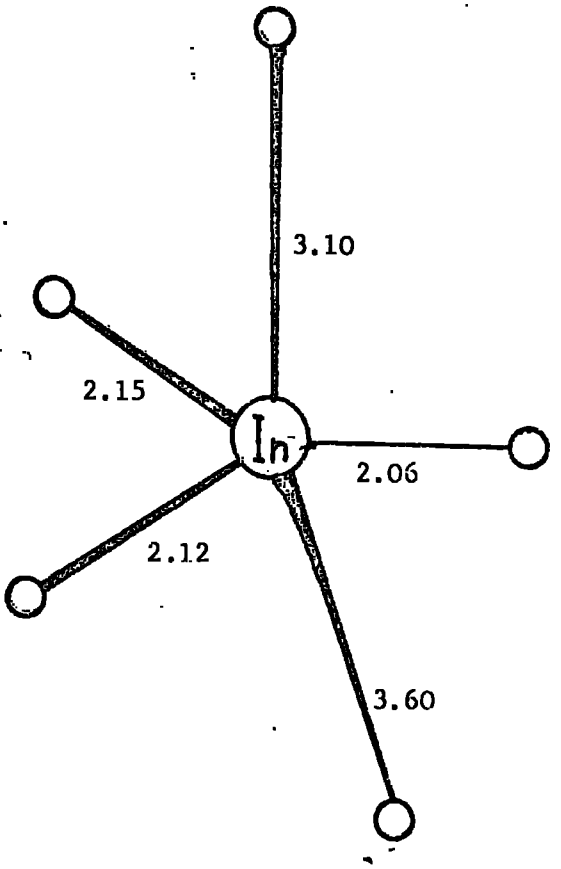
In general the chemistry of trialkyl-gallium compounds closely parallels that of trialkylaluminium compounds with the provisos above. An important difference is that whereas trimethylgallium (and trimethylindium) react with the secondary amines, phosphines and arsines in the order $R_2AsH > R_2PH > R_2NH$, the reverse is true for trimethylaluminium[188].

3.1.5 Me_3In Structure and some Chemical Properties

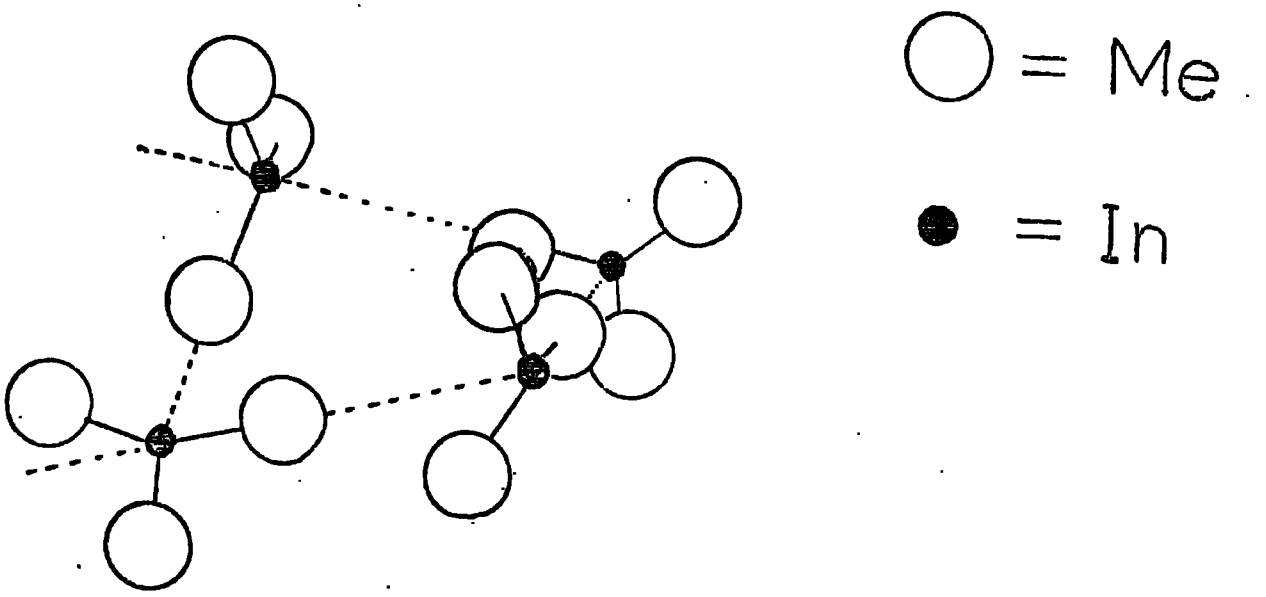
Trimethylindium was first made by L.M. Dennis et al. in 1934 from indium and dimethylmercury[189]. Other, more general methods for the indium alkyls are using Grignard reagents or organo-aluminium or organo-lithium compounds with indium trihalides or the reaction between an alkyl bromide and a Mg-In alloy.

Trimethylindium is a solid at room temperature, forming extremely beautiful crystals, and it has an appreciable vapour pressure (7.2mm. at 30°). Although it is monomeric both in benzene solution[181] and in the vapour phase[190] the associated nature of the compound, suggested by its high

Fig. 2



Me_3In: the arrangement of carbon atoms around the indium atom



The trimethylindium tetramer showing the bridging bonds (broken lines).

E.L. Amma and R.E. Rundle, J.A.C.S., 1968, 80, 4141.

melting point, 88°, has been confirmed by an X-ray analysis[191]. The structure of solid trimethylindium is unusual in that it is a polymeric network of tetramer units held together by long partial bonds. (See Fig. 2). The three nearest neighbours of each indium atom are three methyl groups in a plane so little rearrangement takes place when the crystal vaporizes into monomers. The methyl-indium-methyl bridges are unsymmetrical and within the tetramer unit the In-C distances in the In - C - In bridge, which is nearly linear, are 2.1 and 3.1Å. (The In-C distance in the vapour is 2.16Å)[190]. This exceptional bonding can be explained by the supposition that the methyl groups which take part in these bridges are somewhat flattened in the xy plane, so that both lobes of the $C2p_z$ orbital overlap unequally with the vacant p orbitals of the neighbouring indium atoms.

A proton magnetic resonance study on trimethylindium[192] in various solvents show no appreciable shift of the methyl resonance with either increasing concentration or lowering the temperature to -90°. The associated nature of trimethylindium is thus broken down in solution into monomeric units.

Trimethylindium is spontaneously inflammable in air and is hydrolysed by water, with formation of $MeIn(OH)_2$[86].

$$Me_3In + RH_2O \longrightarrow MeIn(OH)_2$$

This compound has not been studied, but illustrates the difficulty in removing the second or third alkyl groups from indium.

A point of interest with the higher alkyls, which are all monomeric in benzene, is that those in which there is a α-branch in the carbon chain are yellow, e.g. Pr^i_3In. These yellow colours also appear in the thallium alkyls[86].

The chemistry of the organic derivatives of indium have not been as widely studied as the other group III metals up to the present time, probably on account of the high cost of the metal. Generally organo-indium

compounds resemble those of gallium rather than thallium.

The tri-alkyls are weaker acceptors than those of gallium and low valency states are significant for the first time in group III with indium. Cyclopentadienyl indium(I) is a stable compound which does not react with water, but oxidises rapidly in air. It is a linear polymer[193]. (See Fig. 3(b)).

Trimethylindium forms co-ordination complexes with Lewis bases which are slightly less stable than those of trimethylgallium. It reacts with dimethylamine, forming a complex which eliminates methane when heated, yielding the dimer $Me_2In.NMe_2$.

Recently[194] studies of the reactions between trimethylindium and phenylisocyanate have been made. This is shown in (9).

$$Et_3In + PhNCO \longrightarrow Et_2In - \overset{Ph}{\underset{|}{N}} - \overset{O}{\overset{||}{C}} - Et \xrightarrow{H^+} H - \overset{Ph}{\underset{|}{N}} - \overset{O}{\overset{||}{C}} - Et$$

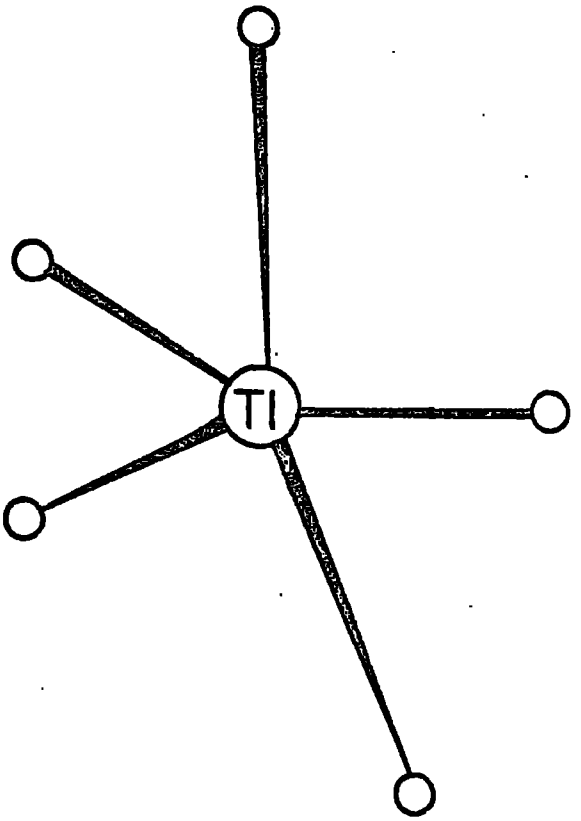
(9)

3.1.6 Me_3Tl Structure and some Chemical Properties

Although the first organo-thallium compound, the air and water stable diethylthallium chloride was made in 1870[195], it was not until 1930 that trimethylthallium was first synthesised from ethyl-lithium and diethylthallium chloride[196] by H.P.A. Groll. The reaction between a Grignard reagent and thallium(III) chloride in diethyl ether stops after the introduction of the second group. The third group can be substituted by carrying out the reaction in tetrahydrofuran[197]. The best way to prepare trimethylthallium is by the reaction of methyl-lithium and thallium (I) iodide in the presence of methyl iodide[198-199]. The overall reaction is:

$$2MeLi + MeI + TlI \longrightarrow Me_3Tl + 2LiI$$

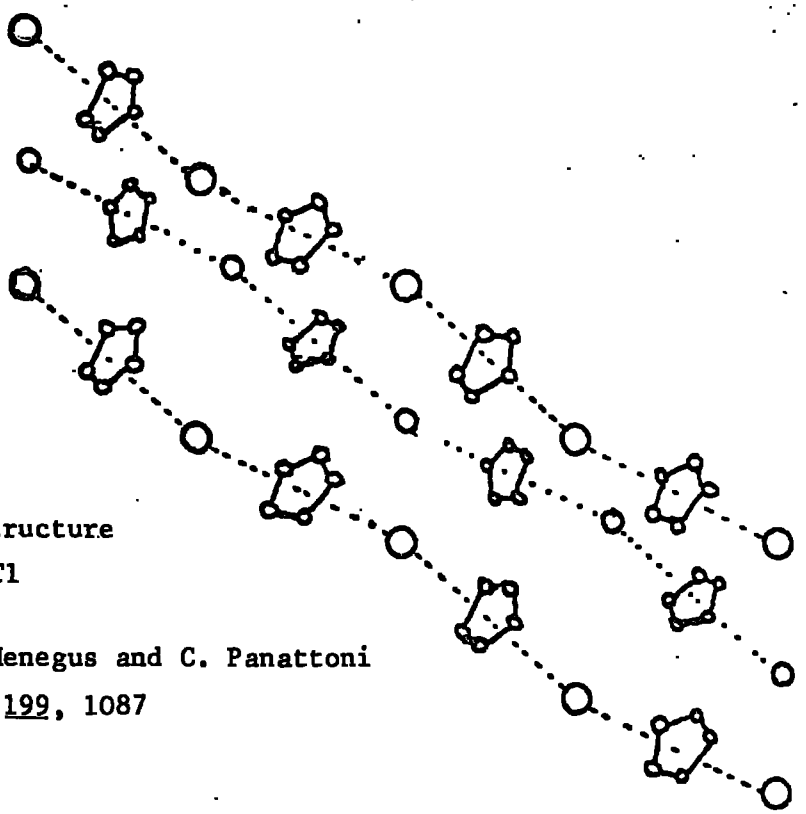
Fig. 3(a) Me_3Tl



The arrangement of carbon atoms around the thallium atom

G.M. and W.S. Shedrick, J.C.S(A), 1970, 28

Fig. 3(b) CpTl, CpIn



The polymeric structure of C_5H_5In, C_5H_5Tl

E. Frasson, F. Menegus and C. Panattoni
Nature, 1963, 199, 1087

The mechanism is proposed thus:

$$MeLi + TlI \longrightarrow LiI + MeTl$$

$$3MeTl \longrightarrow Me_3Tl + 2Tl$$

$$MeTl + MeI \longrightarrow Me_2TlI \xrightarrow{MeLi} Me_3Tl + LiI$$

The finely divided thallium metal can then react with methyliodide:

$$MeI + 2Tl \longrightarrow MeTl + TlI$$

Freezing point measurements show that trimethyl-, triethyl- and triphenylthallium are monomeric in benzene solution[198-200]. Infra-red and Raman studies of trimethylthallium also suggest that it is monomeric in benzene solution and in the vapour phase but that it is associated in the crystal[201]. This has now been confirmed by a single-crystal X-ray study[202]. In the crystal the three nearest neighbours of each thallium are three methyl groups in a plane (see Fig. 3(a)) so that little rearrangement takes place when the crystal vaporises as a monomer. Association to give a polymeric three-dimensional network occurs through unsymmetrical Me-Tl-Me bridges, the coordination about thallium being a distorted trigonal bipyramid with three short equatorial and two long axial bonds.

The methyl bridges are long, 3.2Å, and must clearly be weak in comparison to those in the trimethylaluminium dimer. Although no stable methyl-bridged dimer is formed by trimethylthallium such a dimer has been postulated to be the transition state for intermolecular exchange of methyl groups in solution: this rapid intermolecular exchange is evidenced by the collapse of the doublets due to coupling with ^{205}Tl ($S = \frac{1}{2}$, 70.5%) and ^{203}Tl ($S = \frac{1}{2}$, 29.5%) in the n.m.r. spectrum. The exchange is concentration and solvent dependent, and, being second order in the concentration of Me_3Tl, has been postulated to proceed via a methyl-bridged dimer[203].

The energy of activation is 6 ± 1 kcal.mole^{-1} in CH_2Cl_2. At -70° the exchange could be stopped but all the methyl groups were equivalent in the n.m.r. spectrum so that the bridged dimer can only be a transition state, higher in energy than the monomeric trimethylthallium molecules. The factors governing the formation of dimers include low inter-atomic inner shell repulsion forces and strong electronic configurational interaction (i.e. some sort of metal-metal bond). For thallium the first factor will probably be greater and the second smaller so that dimerisation will be less favourable for thallium than, for example, for aluminium.[204]

Trimethylthallium is pyrophoric and an added hazard in handling the compound is that on heating to about 90° explosive decomposition can occur. Also, due to the weak nature of the Me_2Tl-CH_3 linkage, about 27 kcal.mole^{-1}, trimethylthallium is decomposed by sunlight and must be stored in the dark. Hence trialkylthallium compounds are the most unstable of the Group III alkyls. A recent review[204] by A.G. Lee covers the main details of organothallium chemistry.

The chemistry of the trialkylthallium compounds is dominated by two factors (a) the high stability of compounds of the type R_2TlX, which commonly exist as salts $R_2Tl^+X^-$ and (b) the weakness of the Tl-C bond. The trialkylthallium compounds also continue the trend within group III of being much weaker acceptors than their congenors. For example the Lewis base adduct $Me_3Tl-NMe_3$ is extensively dissociated in the vapour phase[153]. The weak acceptor properties of tri-organothallium compounds have a profound influence on their chemistry in as much as many reactions of organometallic compounds proceed via adduct formation. For example, acetonitrile reacts with Me_3Al via an adduct ($CH_3CN \rightarrow AlMe_3$) to form $Me_2C = NAlMe_2$[205], whereas Me_3Tl is unreactive towards acetonitrile[206]. However with compounds containing acidic hydrogen, not only with methanol

etc., but with less obvious acids such as cyclopentadiene[207], trimethylthallium reacts to form methane and the analogous dimethylthallium derivative[206].

The chemistry of the di-organothallium derivatives is extremely extensive due to their stability and inertness to oxidation, and is generally analogous to the chemistry of the iso-electronic organo-mercury compounds and to the corresponding Tl(I) derivatives, the Me_2Tl moiety behaving as a "pseudo" Tl(I) ion[204]. The di-organothallium moiety is so stable that it requires halogens or interhalogen compounds to cleave the last two metal-carbon bonds.[208]

The general trend to the stability of lower valent states as the group is descended is manifest in organothallium chemistry. Stable thallium(I) compounds such as PhTl and C_5H_5Tl are well known. Cyclopentadienylthallium has a similar structure to cyclopentadienylindium[193] and consists of a long chain polymer (see Fig. 3(b)). No alkylthallium(I) compounds have been isolated. This is not surprising in that the stability of say, C_5H_5Tl is associated with the stability of the cyclopentadienyl anion and C_5H_5Tl is largely ionic. However, due to the lower stability of alkyl anions, alkyl thallium(I) compounds would have to have a largely covalent Tl-C bond. Covalent Tl-C compounds are stabilised by the use of empty p orbitals on the thallium for intermolecular bonding, and as the methyl group has little bridging ability for Tl(III) compounds it is reasonable to assume that Tl(I) alkyls are intrinsically unstable[204].

3.1.7 Mass Spectra of Organometallic Compounds of the Main Group

This section contains a review of mass spectra of relevant compounds of the main group. The extent to which structures can be assigned to ions is quite limited. The high energy of the electron beam (~70eV) means that unimolecular rearrangement processes readily occur and these can

invalidate structural conclusions. Despite these limitations mass spectrometry has provided substantiating evidence for novel compounds as well as being the most definitive method of establishing molecular compositions[209].

In the following review, the mass spectra were produced by electron impact using 50-70eV. Ions in which the number of electrons is odd are represented by $(ion)^{+\cdot}$, whereas even-electron ions are represented as $(ion)^{+}$. This distinction has been found[132] to have considerable significance for main group organometallics, although for transition metal complexes, where ionisation may involve removal of an electron from a non-bonding orbital such considerations are often irrelevant.

3.1.8 Group I

The mass spectra of lithium alkyls are of interest since their vapours contain associated species. For example, ethyllithium vapour gives $Et_5Li_6^+$, $Et_4Li_5^+$, $Et_3Li_4^+$, $Et_2Li_3^+$, $EtLi_2^+$ and Li^+.[210] None of the compounds so far reported[211] produces a molecular ion, but the identity of parent ions can be deduced from appearance-potential measurements of fragment ions. In this way it has been demonstrated that ethyllithium vapour consists of tetramer and hexamer units which decompose on ionisation(I).

$$Et_nLi_n + e \longrightarrow Et_{n-1}Li_n^+ + Et + 2e \qquad (1)$$

$$n = 4 \text{ or } 6$$

Further evidence for the composition of the vapour came from a shift in the ratios of ion intensities as a result of varying the sample temperature. A crystal structure of ethyllithium confirms the existence of association in the solid state[212].

All other ions produced were due to decomposition of the $Et_{n-1}Li_n^+$ species (2).

$$Et_{n-1}Li_n^+ \longrightarrow Et_{n-x-1}Li_{n-x}^+ + (EtLi)_x \qquad (2)$$

Lithiomethyltrimethylsilane, $LiCH_2SiMe_3$[211], vapour produced a spectrum also showing ions, probably derived from tetrameric units, via the ionisation and decomposition processes shown above.

In general in the mass spectra of lithium alkyls, the most abundant ions are Li_2R^+ and ion abundances suggest that the decomposition processes (3) are most favourable when x is even.

$$Li_nR_n^+ \longrightarrow [Li_{n-x}R_{n-x-1}]^+ + Li_x + R\cdot \qquad (3)$$

3.1.9 Group II

The mass spectra of this group of metal alkyls show many trends which reflect changes in ionisation potential and M-C and M-H bond energies.

The mass spectra of R_2Be (R = Me, Et, Pr^n, Pr^i, Bu , or Bu^t)[134,135] have been recorded. With the exception of the di-t-butyl, all beryllium alkyls are associated through Be-C-Be bridging bonds. The low energy of these bridging bonds means that the ion abundances of associated species formed by electron impact will be profoundly affected by source temperature.

This in fact does happen and the most pronounced effect is observed with Et_2Be for which the trimeric fragments $Et_5Be_3^+$ and $Et_4Be_3H^+$ decrease rapidly in abundance as the source temperature is increased from 45^o to 80^o. This behaviour is consistent with increased thermal dissociation of associated molecules at the higher temperatures prior to ionisation. Another trend seen in the mass spectra of R_2Be is the increase in abundance of hydrocarbon ions as the source temperature is raised. This observation is consistent with increased thermal decomposition of di-alkylberyllium compounds at higher temperatures.

The fragmentation of beryllium alkyls reflects the greater stability

of even-electron ions, as in the sequences (4) and (5)

$$Et_4Be_2^{+\cdot} \xrightarrow{-Et^{\cdot}} Et_3Be_2^{+} \xrightarrow{-C_2H_4} Et_2Be_2H^{+} \xrightarrow{-C_2H_4} EtBe_2H_2^{+} \qquad (4)$$

$$R_2Be^{+\cdot} \longrightarrow RBe^{+} + R^{\cdot} \qquad (5)$$

The processes shown above are usually metastable supported, and although the alkene elimination is probably a β elimination process it is not possible to write precise structures for the beryllium-containing product ions. For example, $Et_2Be_2H^+$ could be ethyl- or hydrogen-bridged.

A point of interest in the higher alkyls is that they also show transitions in which C-H and C-C bonds are broken, as indicated by (6) and (7).

$$Bu^t_2Be^{+\cdot} \longrightarrow Bu^tBeCMe_2^{+} + Me^{\cdot} \longrightarrow Bu^tBe^{+} + C_3H_6 \qquad (6)$$

$$C_3H_7Be^{+} \xrightarrow{-H_2} C_3H_5Be^{+} \xrightarrow{-H_2} C_3H_3Be^{+} \qquad (7)$$

Alkane elimination from odd-electron monomer ions is a favoured process (8) in marked contrast to the behaviour of the group IVa metal alkyls.

$$(C_nH_{2n+1})_2Be^{+\cdot} \longrightarrow C_nH_{2n}Be^{+\cdot} + C_nH_{2n+2} \qquad (8)$$

The compounds Me_2Zn[212], $(t\text{-}Bu)_2Zn$[213], Me_2Hg, Et_2Hg and $(n\text{-}Bu_2)Hg$[214] have been examined. All give $MR_2^{+\cdot}$, MR^+ and M^+ ions in high abundance, indicating that the major decomposition processes are bond cleavages (9).

$$R_2M^{+\cdot} \longrightarrow RM^{+} \longrightarrow M^{+\cdot} \qquad (9)$$

Hydride ions RMH^+ and MH^+ ions are present in extremely low abundance. Hydrocarbon ions are major species in the spectra of the mercury compounds but may arise from thermal decomposition before ionisation.

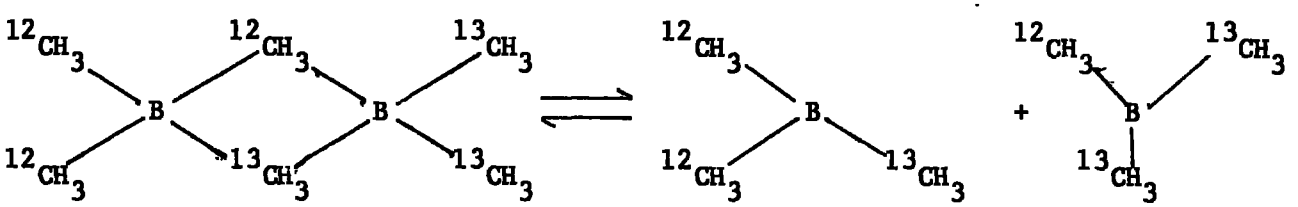
The ionic cyclopentadienyl, $(C_5H_5)_2Mg$, gives a similar spectrum to

$(C_5H_5)_2Mn$, producing fragment ions $C_5H_5M^+$ and M^+ of high abundance formed by metal-ring bond cleavage[215]. The bis-cyclopentadienyls of transition metals produce similar fragment ions although in different relative abundances and the molecular ion is generally the most intense[209,215].

3.1.10 Group III

The mass spectra of trimethylborane and other alkylboranes have been examined at[216,217] unspecified but presumably high source temperatures. The most abundant species is the BR_2^+ ion with low abundances of the molecular ion $R_3B^{+\cdot}$ and the B^+ ion. The mass spectra of Me_3B will be considered more fully in the Discussion of this thesis (Section 3.4).

An interesting study was made[216] using ^{13}C in an attempt to discover if Me_3B associated at low temperatures. By introducing $(^{13}CH_3)_3B$ into $(^{12}CH_3)_3B$, and by freezing down and then examining the mass spectra it was shown that no "scrambling" of the $^{13}CH_3$ groups took place and so a dimer-monomer equilibrium such as (10) does not take place.



(10)

The mass spectroscopic studies on trimethylaluminium and other aluminium alkyls indicate the importance of source temperature and sample introduction techniques when dealing with reactive air-sensitive compounds. Previous studies[212,218], on trimethylaluminium and other bridge-bonded aluminium alkyls have had a source temperature of around 200°. Trimethylaluminium gives Al^+, $AlCH_3^{+\cdot}$, $AlMe_2^+$ and $AlMe_3^{+\cdot}$ as the most abundant metal-containing species. Rearrangement ions AlH_2^+ and $HAlMe^{+\cdot}$ are of low

abundance.

From clastograms (plots of ion current vs. electron energy) and appearance potentials of the major ions it maybe deduced that simple bond cleavage decomposition of the parent ion occurs (11)

$$AlMe_3^{+\cdot} \longrightarrow AlMe_2^{+} \longrightarrow AlMe^{+} \longrightarrow Al^{+} \qquad (11)$$

Although trimethylaluminium is known to be dimeric in the vapour phase, these studies[212,218] detected $Al_2Me_5^+$ as the only bi-aluminium species and then in extremely low abundance.

A more comprehensive study of Me_3Al, Me_2AlH, Et_3Al, Et_2AlH and Et_2AlOEt at low and high source temperatures[132,133] shows that, in Me_3Al for example, the dimeric ions $Me_5Al_2^+$ and $Me_2Al_2^+$ are quite abundant at source temperatures of ca. 40° and their abundance deminishes rapidly with increasing source temperatures.

The behaviour of associated species in the spectra of alkylaluminium compounds thus closely parallels that of the alkylberyllium compounds.

Thermal decomposition also takes place as the source temperature is increased.

The spectrum of dimethylaluminium hydride is of some interest not only because of trimeric and dimeric ions in its vapour, but also because above a source temperature of 100° thermal rearrangement to Me_3Al was observed. This rearrangement is probably due to methyl exchange from one aluminium to another.

Diethylaluminium hydride also rearranges with increasing source temperature to triethylaluminium.

The fragmentation behaviour of organoaluminium compounds is similar to organo-derivatives of group IV apart from the above features. All the compounds produce parent monomer ions and even-electron aluminium containing ions are far more abundant than odd-electron ions.

Trimethylaluminium fragments mainly by loss of methyl radicals but metastable peaks are observed for more complex rearrangement processes such as (12) and (13)

$$Me_2Al^+ \rightarrow H_2Al^+ + C_2H_4 \qquad (12)$$

$$Me_2Al^+ \rightarrow Al^+ + C_2H_6 \qquad (13)$$

For the ethyl compounds elimination of ethylene from even-electron ions is a major process and the high abundance of H_2Al^+ ions in the spectra can be ascribed to (14).

$$Et_2Al^+ \longrightarrow EtAlH^+ \longrightarrow H_2Al^+ \qquad (14)$$

One respect in which aluminium alkyls differ from their beryllium analogues is that dimer ions decompose to some extent by elimination of neutral R_3Al species (15), (R + H, MeEt)

$$Et_2AlH_3^+ \longrightarrow Et_2Al^+ + AlH_3 \qquad m^* = 62.8 \qquad (15)$$

whereas the beryllium alkyls lose an alkyl radical[134].

3.1.11 Group IV

The mass spectra of the organo-derivatives of Group IV have been the subject of an extensive literature[2,132,209,219]. The following review contains only the relevant points of the spectra.

The mass spectra of the group IV alkyls have many features in common, and the differences observed are qualitatively related to the decrease in ionisation potential of the metal with increasing atomic number and to a progressive decrease in the metal-carbon and -hydrogen bond strengths. For example, metal hydride ions are least abundant with lead, and Et_4Pb

eliminates butane from the Et_3Pb^+ ion whereas a similar process is rarely observed with the lighter members of the group. Molecular ions generally are of low abundance and radical elimination by M-X bond cleavage (16) is a dominant decomposition path for molecular and other odd-electron ions.

$$R_4M^{+\cdot} \longrightarrow R_3M^+ + R^\cdot \qquad (16)$$

In unsymmetrical molecules such as R_3MR', the radical most readily eliminated is that which is most weakly bonded to the metal in the neutral molecule whilst similarly in metal-metal bonded complexes of the type $R_3M{\cdot}M'R'_3$ (M,M' = Si, Ge, Sn) extensive cleavage of the metal-metal bond occurs only when it is the weakest bond in the neutral molecule. In methylpolygermanes, $Me_{2n+2}Ge_n$, loss of a methyl radical is followed by successive elimination of Me_2Ge units. Cyclic organosilanes, $(Me_2SiCH_2)_3$, produce only one major fragment ion due to the loss of methyl from the parent while linear silanes of the type $Me_3SiCH_2(SiMe_2CH_2)_{0-2}SiMe_3$ fragment by cleavage of methylene-silicon bonds.

Radical elimination from even-electron ions is rarely observed and only a few examples are metastable-supported (17) and (18).

$$Ph_2GeMe^+ \longrightarrow Ph_2Ge^{+\cdot} + Me^\cdot \qquad (17)$$

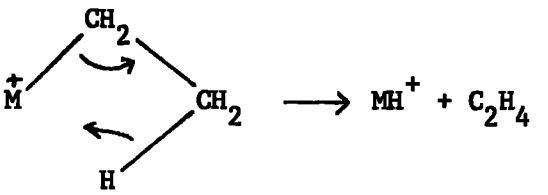
$$PhSn^+ \longrightarrow Sn^{+\cdot} + Ph^\cdot \qquad (18)$$

Due to the weakening M-C bond as the group is ascended and the comparability in strength of the Si-C and M-C bonds, cleavage of C-C and C-H is most apparent with organosilanes, although tolylgermanes produce ions owing to methyl loss.

Alkene elimination is an important fragmentation process for all σ-bonded metal alkyls, frequently metastable-supported. It is a general reaction for even-electron ions containing the grouping R_2CHCH_2M and is

probably a β-elimination process (19).

$$Et_3M^+ \xrightarrow{-C_2H_4} Et_2MH^+ \xrightarrow{-C_2H_4} EtMH_2^+ \xrightarrow{-C_2H_4} MH_3^+ \qquad (19)$$



Alkene elimination from odd-electron parent ions has not been observed; on mechanism (19) it requires a pentaco-ordinate intermediate which may be energetically unfavourable compared with radical elimination.

Molecule elimination by cleavage of two M-X bonds is most favourable for the heavier molecules and comparatively few organosilanes show metastable peaks for alkane and hydrogen elimination. This again reflects the M-C and M-H bond energy changes in the group.

Finally many low abundance ions are formed by processes which do not involve cleavage of bonds to the metal. For example, the higher alkyls eliminate smaller alkene fragments (20) and phenylmetal ions degrade partly by successive elimination of acetylene (21).

$$C_3H_7M^+ \longrightarrow CH_3M^+ + C_2H_4 \qquad (20)$$

$$PhM^+ \xrightarrow{-C_2H_2} C_4H_3M^+ \xrightarrow{-C_2H_2} C_2HM^+ \qquad (21)$$

This latter is a high energy process which disappears at 20 eV and diminishes in the order Si>Ge>Sn>Pb.

3.1.12 Group V

For triphenyl derivatives[220] molecular ion abundances diminish in the order As>Sb>Bi whereas metal ion abundances M^+ follow the reverse order, as expected from the variation of M-C bond strengths within the group.

Similar observations concerning M^+ ions maybe made for the trimethyl compounds [212].

Of these compounds Me_3Sb has been studied in most detail [212] and clastograms and appearance potential measurements on the major ions $Me_3Sb^{+\cdot}$, Me_2Sb^+, $MeSb^{+\cdot}$ and Sb^+ indicate simple bond cleavage decompositions. (22).

$$Me_xSb^+ \longrightarrow Me_{x-1}Sb^+ + Me^\cdot \qquad (22)$$

Loss of H_2 (or $2H^\cdot$) from R_2M^+ ions is observed for all arsenic and antimony compounds but not the bismuth [212].

3.1.13 Appearance Potentials and Thermodynamic Data

The first ionisation potential of a molecule is defined as the energy difference between the ground-state vibrational level, of the lowest electronic state of the molecule, and the molecular ion.

The conditions under which ionisation takes place are governed by the Franck-Condon principle in that the electron-bombardment interaction time is so short (10^{-15} sec.) compared with the vibration time (10^{-12} to 10^{-13}sec.) that nuclei may be considered as fixed at their equilibrium distances during the ionisation process. The potential energy curves plotted thus resemble the "potential well" concept, and the transition is referred to as a vertical transition and the ionisation potential measured in this way as the vertical ionisation potential.

It can be seen that the ionisation potentials obtained by electron impact methods are upper limits and the appearance potentials (i.e. the potential at which an ion first appears) will also give upper values of bond strengths.

The experimental problem in measuring appearance potentials is to find accurately the intercept, on the voltage axis, of graphs of ion current versus the ionising electron voltage, (ionisation efficiency curve),

The shape of these curves is well established. With decreasing voltage the curve increases to a maximum value followed by a region of linear decrease. The curve then approaches the energy axis almost exactly exponentially, due to the "geometry" of the potential well itself and a non-mono-energetic electron beam. Normally a mass spectrometer source forms the electron beam by acceleration of electrons emitted from a hot filament. The energy distribution of the emitted electrons will be essentially Maxwellian[221,222] and thus even when the minimum value of the electron energy is equal to the appearance potential of a molecule, appreciable ion current persists because appreciable numbers of electrons with higher energies results.

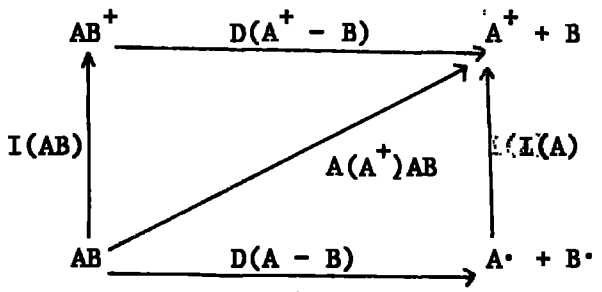
In addition to difficulties arising from the shape of the curve, there are other sources of error in the measurement of appearance potentials using mass spectrometry. These have been extensively discussed[132,233] and the main points summarised below.

The occurrence of a potential gradient within the ionisation chamber leads to the electrons being given an extra increment of energy. If the repeller voltage is kept constant however this effect should not lead to a difference between two ionisation potentials. Magnetic scanning must also be used if the field in the ion chamber is to be the same for the examination of two ions of different mass. The trap should be at the same potential as the ionisation chamber to minimize energy increments and the filament temperature should be constant as variation in temperature causes an energy spread in the electron beam.

Although there have been several methods of finding the true origin of the ionisation efficiency curve and hence the appearance potential, the best method is due to Warren[224]. In this method, which uses an internal standard of known ionisation potential, the ion current scales for the two

current scales are adjusted so as to make the straight line portions parallel. The difference in voltage between corresponding ion currents on the curves is plotted against ion current and from the voltage difference at zero ion current the appearance potential is found. The objection to this method is that the shape of the two curves may not be the same very near to the potentials at which the two currents vanish.

Heats of formation and bond dissociation energies may be obtained from appearance potentials and ionisation potentials and/or calorimetric data. Ionisation by electron impact and subsequent fragmentation of the molecular ion by bond cleavage may be represented in the following cycle.



where $I(A\cdot)$ = ionisation potential of $A\cdot$

$A(A^+)AB$ = appearance potential of A^+ from AB

$D(A - B)$ = dissociation energy of bond A - B

From this cycle the following relationships may be obtained:

$$A(A^+)AB = IAB + D(A^+ - B) + E_1$$

$$A(A^+)AB = I(A) + D(A - B) + E_2$$

The terms E_1 and E_2 represent excess kinetic energy of the dissociation plus any excitation energy of the products A^+ and $B\cdot$. A simplifying assumption is that E_1 and E_2 are zero, i.e. that both the ion and the radical are in the ground state but as has been said this is not necessarily so. The validity of using appearance potential measurements for the derivation of thermodynamic quantities depends on the correct assignment of the process

involved in the threshold measurement.

From the above it can be seen that a knowledge of the ionisation potentials of intermediate radicals is required before intermediate bond energies are obtained. Relative bond energies may still be calculated however without knowledge of ionisation potentials. If for the compounds $L_nM\text{-}R$ the appearance potential of L_nM^+ is measured then by a subtraction of the two equations,

$$A(L_nM^+)L_nM\text{-}R_1 = IL_nM + D(L_nM\text{-}R_1)$$

$$A(L_nM^+)L_nM\text{-}R_2 = IL_nM + D(L_nM\text{-}R_2)$$

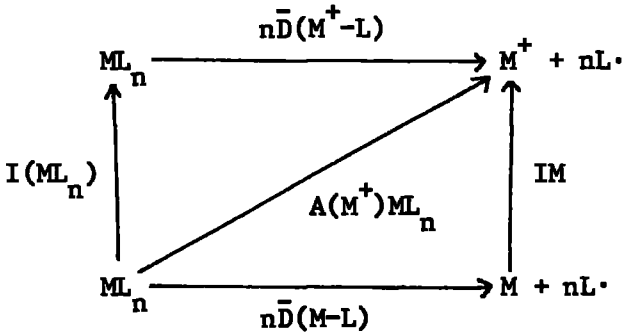
bond dissociation energy differences are found.

$$D(L_nM\text{-}R_1) - D(L_nM\text{-}R_2) = A(L_nM^+)L_nM\text{-}R_1 - A(L_nM^+)L_nM\text{-}R_2$$

Mean metal-carbon bond dissociation energies for an ML_n compound (M is a metal and L is a ligand) may be calculated if we assume that the appearance potential of M^+ is the energy required for the decomposition

$$e + ML_n \longrightarrow M^+ + nL\cdot + 2e$$

Assuming no excess energy release, the cycle below may be written:



$\bar{D}(M\text{-}L)$ = mean dissociation energy of M-L bond in ML_n

$\bar{D}(M^+\text{-}L)$ = mean dissociation energy of M-L bond in ML_n^+

From this the bond energies in the molecule and the molecular ion

$$\bar{D}(M\text{-}L) = \frac{1}{n}\left[A(M^+)ML_n - I(M)\right]$$

$$\bar{D}(M^+\text{-}L) = \frac{1}{n}\left[A(M^+)ML_n - I(ML_n)\right]$$

can be calculated.

3.2 Experimental

3.2.1 Preparation and Purification of Compounds

Trimethylboron

Trimethylboron was prepared[86,144] by slowly adding a solution of boron trifluoride etherate, 2.8g., 0.019M, in di-n-butylether, 10ml. to a solution of trimethylaluminium, 1.33g., 0.019M, in di-n-butylether, 10ml. at 0°. The mixture was stirred for one hour at 20°, nitrogen being passed through the apparatus into a -196° trap. The contents of the trap were then transferred to a fractionation train and pumped through two -112° traps and into a -196° trap. The final product contained a trace of Me_2BF (mass spectrometry), which was eliminated by pumping at -155°.

Trimethylgallium

Some samples of trimethylgallium were kindly supplied by Dr. A.J. Downs of the University of Oxford. These were contaminated however, by small amounts of Me_2Hg, detected by high resolution mass spectrometry. More trimethylgallium was made by condensing dimethylmercury (from MeMgBr and $HgCl_2$[225]) onto excess gallium metal and a trace of MeHgCl[176], in an all-glass apparatus with boiler and a condenser containing Fenske helices, attached to the vacuum line. The apparatus was let down to argon, 360mm. Hg at 20°, and the boiler heated at 90°-120° for one week. The argon was then pumped off and all the volatiles at -40° were transferred to the fractionation train and pumped through two -78° traps into a -196° trap. The criterion of purity used, was the vapour pressure of the sample.

Both the vapour pressure equations of dimethylmercury and trimethylgallium are known,[86,226]

Me_2Hg	Me_3Ga
$\log_{10} p_{mm.} = 7.575 - \frac{1720}{T}$	$\log_{10} p_{mm.} = 8.07 - \frac{1705}{T}$

and so by repeated fractionation through -78° traps eventually a sample of Me_3Ga was obtained which had a vapour pressure of 169.5mm. Hg. (170.2mm. theoretical) at 19°. This was then transferred via a -40° trap (in order to condense out mercury) into a double break-seal apparatus. Even this sample contained a slight trace of Me_2Hg under high resolution mass spectrometry and so another approach was made. Gallium trichloride was made by gently heating gallium metal in an atmosphere of dry hydrogen chloride diluted with nitrogen, distilling out the $GaCl_3$ and then re-subliming. A quantity, 2g. of $GaCl_3$ was then weighed out in a glove box into a break seal apparatus which was then sealed onto a vacuum line, evacuated and excess pure Me_3Al, 5ml., condensed on. On warming to 20°, heat was evolved and the white solid dissolved. The reaction mixture was warmed gently to 40° and left for 12 hours, transferred to a fractionation train and pumped through two -60° traps into a -196° trap. The -196° fraction had a vapour pressure of 179.5mm. at 20° (required for Me_3Ga, 178.2mm.). This was transferred via a -40° trap into a break-seal apparatus.

Tri-vinylgallium

This was made by the method of J.P. Oliver and L.G. Stephens[182]. Di-vinylmercury, 3g., 0.01M, (from vinylmagnesium bromide and mercuric chloride in T.H.F.[227]), dried and twice distilled b.p. 156°, was condensed onto gallium metal 2g., 0.03M, in an all-glass apparatus attached to the vacuum line. The reaction mixture was left at 20° for 12 hours and then stirred. The products were then pumped through a -23° trap into a -196° trap. The -23° trap was sealed off and contained tri-vinylgallium.

Trimethylindium and trimethylthallium

These were available in a pure state in the laboratory.

3.2.2 Recording Mass Spectra

Spectra were recorded on an A.E.I. MS902 double-focussing instrument. Routine measurements, such as high resolution mass measurements, were carried out as described in the instruction manual and unless otherwise stated, ions were produced under the following conditions:

Ionising electron beam voltage = 70eV

Accelerating voltage = 6kV

Source temperature = 30^{o} to 270^{o}

The author wishes to thank Mr. G. Jordan and Mr. R. Spratt of the Chemistry Department, The Queen's University of Belfast for recording the mass spectra.

Since some difficulties were encountered with various methods of sample introduction and the production of reproducible spectra for abundance measurements, these are discussed in detail below.

3.2.3 Sample Handling Systems

Electron impact sources require sample vapour at a pressure of about 10^{-5}mm. The usual approach is to maintain a pressure of about 10^{-2}mm., in a large reservoir from which vapour passes to the source through a leak which reduces the pressure to 10^{-5}mm. The sample reservoir is filled by (a) a "cold inlet" system whereby an aliquot of the gas/vapour is expanded, into the 2 litre reservoir; (b) a drop of the liquid is introduced via a gallium covered sinter into a reservoir (this system can be heated to cause vapourisation) or (c) for very involatile liquids the sample is introduced into a thimble, evacuated and then heated until the required vapour pressure is reached. With the trialkyl compounds of the group III elements the above methods have obvious disadvantages. The alkyls are all highly air-sensitive and of course relatively unstable. Heating at 200^{o} in a reservoir probably contaminated with various metallic residues which could

either catalyse decomposition or cause anomalous ions, is clearly unsuitable.

To overcome these difficulties, an all-glass inlet system was attached to the mass spectrometer (Fig. 4). As all the group III alkyls are volatile at ordinary temperatures, the rate of evaporation of material into the source was controlled by the temperature of the sample.

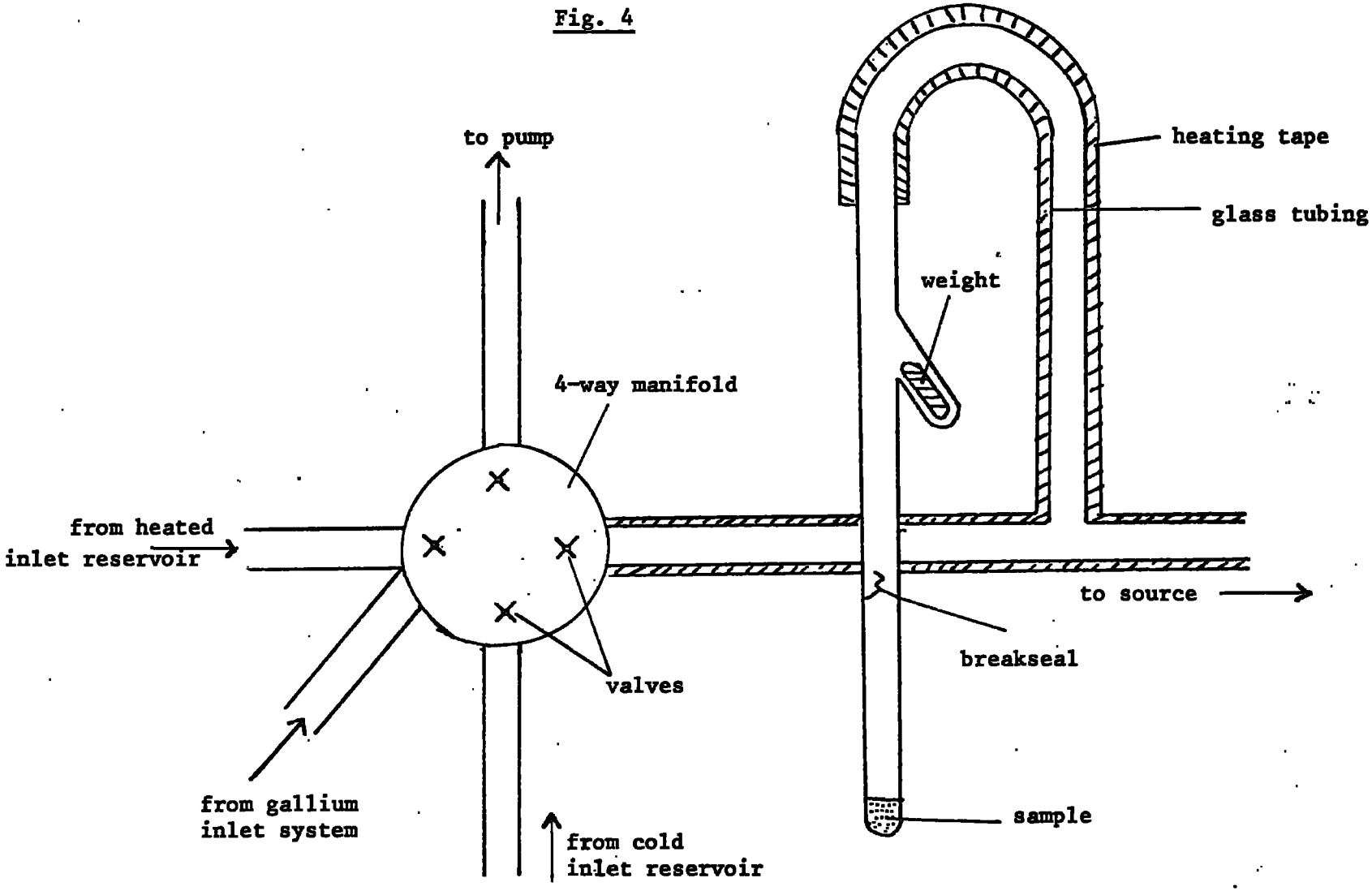
To give a reading on the source ionisation gauge of 2-8 x 10^{-6}mm. the following sample temperatures were required: Me_3B -155°, Me_3Ga -90° to -80°, Me_3In -20° to -15° and Me_3Tl -15° to 0°.

The following procedure was adopted in all cases. The sample was introduced into a break-seal apparatus, containing a glass-coated beaker (to avoid possible catalytic decomposition by metal), from a vacuum line. The apparatus was then glass-blown onto the inlet system. The inlet system (but not the sample) was heated at 250° under "hard" vacuum for 48 hours prior to the seal being broken and readings taken. After the experiment the apparatus was sealed off.

3.2.4 Obtaining Spectra for Abundance Measurements

These were recorded using a resolution of 1 part in 5,000 and a source pressure not so high that "sparking" of the high voltage employed in the source occurred. Also it is important that a constant monitor current (i.e. a quantity proportional to the total ion current issuing from the ionisation chamber found by intercepting part of the ion beam before it enters the magnetic sector) prevails while the spectra are recorded if meaningful abundances are to be obtained. Some manipulation of the temperature of the cooling baths around the sample was necessary for this condition to be met.

Fig. 4



DIRECT EVAPORATION INLET SYSTEM

3.2.5 Measurement of Appearance Potentials

While an appearance potential is being measured it is essential that a constant monitor current prevails (i.e. for about thirty minutes). Thus the direct evaporation inlet system was used.

After the sample which produced an ion whose appearance potential (A.P.) was to be measured had been introduced into the mass spectrometer, argon was introduced via the "cold inlet" system. The following procedure was then adopted. The $Me_2{}^{69}Ga^+$ peak (for example) was first tuned, by adjusting the magnetic field, onto the collector meter and the ion beam focussed to its maximum value with the ion repeller voltage set between -1.0 to +5 volts, the electron beam voltage at 20V., and the trap current at 20μA. The electron beam voltage was increased to 25eV and the ion currents given on the collector meter for the two ions $Me_2{}^{69}Ga^+$ and Ar^+ were adjusted to give equal values by altering either the sample temperature or the argon pressure.

Since the accuracy of A.P. measurements depends on the sensitivity of ion detection this was made as great as possible by using:

(a) a high source pressure produced by sample and standard of about $7\text{-}8 \times 10^{-6}$mm. "Sparking" must not occur while measurements are in progress as this alters potential gradients within the source;

(b) the source slits were opened to give a resolution of 1:1,000. For optimum results a resolution of 1:500 is used, but because of the co-existence of $C_2H_4{}^{71}Ga$ at m/e = 99 a lower resolution was not possible.

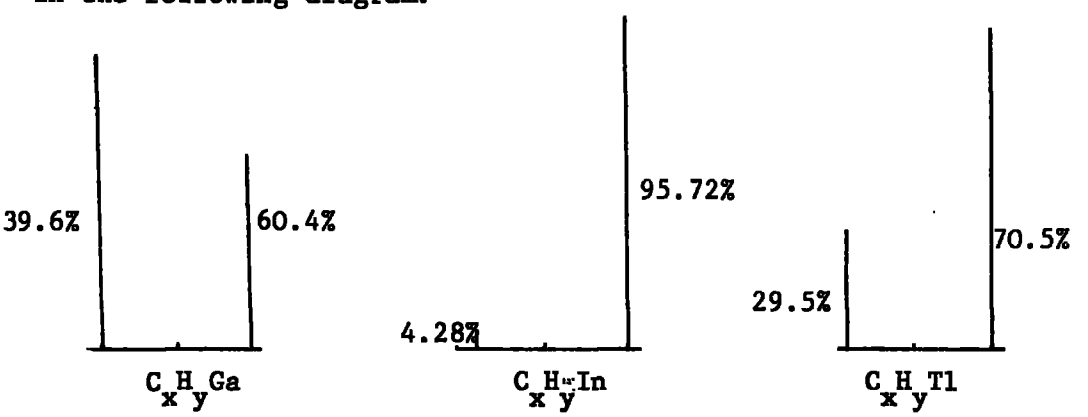
The electron beam was then reduced to 20V and then the ion multiplier voltage was increased until the $Me_2{}^{69}Ga$ gave a reading of 5 to 7 x 1,000 units on the meter. Having made sure that the collector meter reads zero at 5eV (well below the A.P. of the ions), and the ion beam correctly focussed, the voltage was decreased in 0.2V steps and the ion currents for

$Me_2{}^{69}Ga^+$ and $Ar^{+\cdot}$ measured after each step. The meter was zeroed periodically and readings of ion currents discontinued, when they became less than 0.5 x 1 units. A graph could then be drawn of ion current against eV and the linear portion of the ionisation efficiency curve established. When the two ions were no longer being formed the voltage was increased to 20eV and ion currents again read and checked with the initial readings. If there was any discrepancy the set of readings was discarded. Appearance potentials were determined from three sets of measurements using methods described in 3.1 of this thesis.

3.3 Calculation of Results

3.3.1 Identification of Ions

The mass spectra of the Group III organometallic compounds are, with the exception of aluminium, complicated slightly by the presence of poly-isotopic metal ions, and characteristic patterns are produced for each metal-containing ion which reflect the isotope abundances of the metal, as in the following diagram.



The characteristic patterns produced by ions containing a poly-isotopic metal or metals are useful in allowing an immediate recognition of metal-containing ions and the determination of the number of metal atoms in an ion from the low resolution spectrum. Sometimes, however, the pattern produced by a major ion often hides the presence of a low abundance ion only a few mass units different. For example, $^{69}Ga^{12}CH_2$ and $^{71}Ga^{12}C$ will both appear at m/e = 83 and the characteristic gallium pattern will not be seen. Although, often it is possible to identify overlying ions from the low resolution pattern produced, the identification of ions present in a spectrum is more easily accomplished by measuring the precise masses of ions to seven significant figures.

The empirical formulae of all metal-containing ions in this thesis were established by precise mass measurements. The agreement between measured and calculated mass was in the majority of cases better than 5 p.p.m. and always better than 9 p.p.m., (see Appendix 1).

3.3.2 Calculation of Abundances

For ions containing monoisotopic elements, abundances are found quite easily from peak heights produced by the ions in the low resolution spectra. Thus if A^+ is of peak height four arbitrary units (a.u.), B^+ 3 a.u., C^+ 2 a.u. and D^+1 a.u., the abundance of A^+ as a percentage of total ion current is 40%. In comparing the abundances of ions containing polyisotopic elements with other types, contributions from each isotope combination must be summed. For example a spectrum showing three peaks of relative height 2:1:1 due to $^{127}I^+$, $^{81}Br^+$ and $^{79}Br^+$ corresponds to a 1:1 ratio of I^+ to Br^+.

In calculating the abundances of ions allowance has been made for ^{13}C. The natural abundance of ^{13}C is 1% and for ions containing n carbon atoms, n% of the ions will contain a ^{13}C atom. Thus if the effects of ^{13}C are neglected, the abundances of ions containing a large number of carbon atoms, will be underestimated. The effect ^{13}C can have on a mass spectrum is shown in the mass spectrum of trimethylboron. The ion $^{12}C_2H_6B^+$ is of such a large abundance that the ion $^{12}C^{13}CH_6B^+$ is also present in medium abundance. High resolution techniques are needed to differentiate this ion from the possible $C_2H_7M^+$ ion.

Generally, in the mass spectra of the group III alkyls most of the ion current, 90-95%, is carried by metal-containing ions.

Ion currents are measured in arbitrary units (a.u.) which depend on sample pressure in source and on instrument sensitivity of ion detection while the spectrum is being recorded. Abundances on the other hand are dimensionless and are hence not dependent at least to a first approximation, on instrument sensitivity. To calculate the abundances of ions which appear at the same nominal mass, the following procedure was adopted. In the mass spectrum of trimethyl-gallium between m/e = 81 and m/e = 87 there is a cluster of ions identified from high resolution

mass spectrometry.

Nominal Mass	Ion
81	$^{69}Ga^{12}C$
82	$^{69}Ga^{12}CH$
83	$^{69}Ga^{12}CH_2$, ^{71}GaC
84	$^{69}Ga^{12}CH_3$, $^{71}Ga^{12}CH$
85	$^{69}Ga^{12}CH_4$, $^{71}Ga^{12}CH_2$
86	$^{71}Ga^{12}CH_3$
87	$^{71}Ga^{12}CH_4$

Suppose that the peak height at 81 is x a.u. and the peak height at 83 is y a.u. Now the peaks at 81 and 83 consist only of $^{69}Ga^{12}C$, $^{69}Ga^{12}CH_2$ and $^{71}Ga^{12}C$ from high resolution mass spectrometry.

The natural abundance of ^{69}Ga is 60.4% and that of ^{71}Ga is 39.6%. Hence the total abundance of $^{69}Ga^{12}C$ and $^{71}Ga^{12}C$ is (x/0.604) a.u. and hence the abundance of $^{69}Ga^{12}CH_2$ is (y - x/0.604) a.u.

By working through the range of peaks thus, total ion abundances may be obtained.

When there were complications in using the above method another procedure was used. This was to use the oscilloscope on the mass spectrometer and estimate the areas of the adjacent peaks under high resolution.

3.3.3 Assignment of Metastable Peaks

The phrase "metastable peaks" is used for peaks arising in the mass spectra due to decomposition of metastable ions during their flight through the mass spectrometer tube[228]. They are recognisable not

only from the fact that they appear at non-integral mass numbers but also because they are imperfectly focussed compared with peaks due to ions which travel the whole length of the spectrometer without decomposition.

Because of the directional focussing properties of the sector magnetic field the decomposing ions most likely to be recorded are those which undergo the transition in the field free region preceding the magnetic analyser. For the decomposition

$$m_1^+ \longrightarrow m_2^+ + (m_1 - m_2)$$

with internal energy release TeV the position of maximum intensity for the observed metastable peak covers a mass range[229] given by

$$m^* = \frac{m_2^2}{m_1}\left[1 \pm \left[\frac{m_1 - m_2}{m_2} \cdot \frac{T}{eV}\right]\right]^{\frac{1}{2}}$$

where V is the accelerating voltage between the ionisation chamber and entrance slit to the electrostatic analyser. For most metastable decompositions however the internal energy release is small enough to be neglected and the position of maximum intensity is given by

$$m^* = \frac{m_2^2}{m_1}$$

Although the shape of metastable peaks is generally roughly gaussian the peaks often differ widely in width and factors such as finite beam dimensions, angular spreading and kinetic energy of separation of fragments and discrimination against production must be considered for a complete analysis[230].

The values m_1 and m_2 associated with any metastable peak m* can usually be determined by trial and error, remembering that the apparent mass is smaller than either of the masses of the "parent" and "daughter"

peaks and that the peaks at m_1 and m_2 will be much larger than the metastable peak.

Of great help in this respect are tables of m* values that occur for various values of m_1 and m_2 ($m_1 \leqslant 500$ and $500 \geqslant m^* \geqslant 1$) [231].

With polyisotopic elements present in an ion, metastable peaks produced by the decomposition of such an ion eliminating a neutral species consisting of essentially monoisotopic elements (e.g. a hydrocarbon) must follow the peak pattern of the daughter and parent ions.

For example in the mass spectrum of Me_3Ga there are two large metastables at 49.9 and 48.1 due to the following transitions

$$Me_2{}^{71}Ga^+ \longrightarrow {}^{71}Ga^+ + C_2H_6 \qquad m^* = 49.9$$

$$Me_2{}^{69}Ga^+ \longrightarrow {}^{69}Ga^+ + C_2H_6 \qquad m^* = 48.1$$

3.4 DISCUSSION

The high resolution mass spectra of the group III metal alkyls, trimethylboron, trimethylgallium, trimethylindium and trimethylthallium were run at low source temperatures using a direct all-glass inlet system. Of the group III alkyls only trimethylaluminium had previously been shown to be associated in the vapour phase (see section 3.1).

As a subsidiary experiment the high resolution mass spectrum of trivinylgallium (which had previously been shown to be associated in solution[182]) was also run at low source temperature. The metal-containing ions found in the mass spectra are shown in Fig. 5 and 6 (See Appendix 1 and 3 for accurate masses).

3.4.1 Associated Species

The absence of any associated species in the mass spectra of the vapour phase of trimethylboron confirmed previous results[216,217]. No associated species were found also in the vapour phase of trimethylindium and -thallium although both of these compounds exist in the solid state as tetramers[191,202].

However, in two samples of trimethylgallium (supplied by Dr. A.J. Downs of Oxford University) small abundances (<0.1%) of the trimer ion $(Me_3Ga)_3^{+\cdot}$ and the dimer species $Me_3Ga_2^+$ were unambiguously identified by accurate mass measurements and isotope patterns. (see Fig. 7).

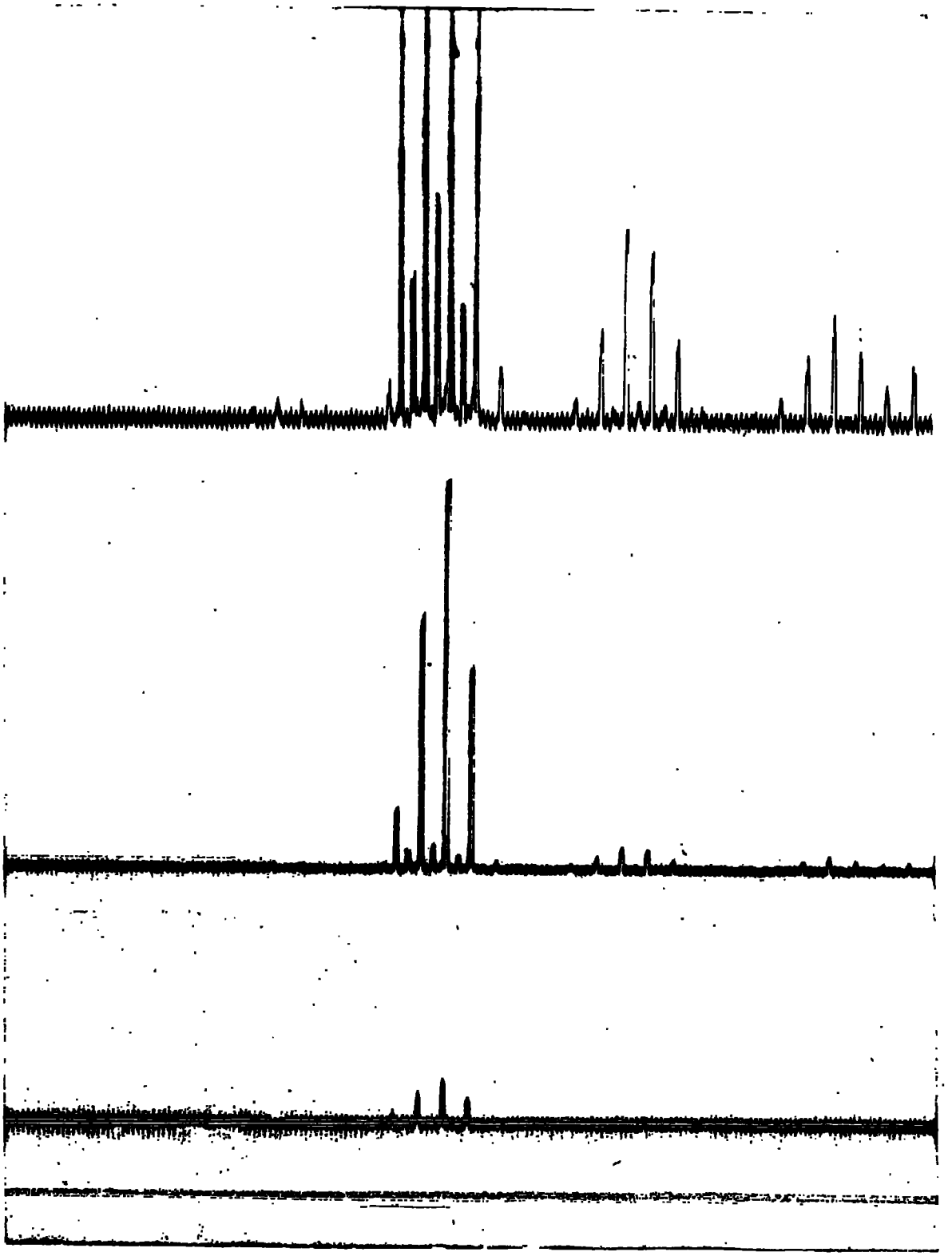
These associated species were heavily dependent on a low source temperature and high sample pressure (6×10^{-6} mm. Hg) and disappeared rapidly with increasing source temperature (Fig. 8(a)). The two samples containing the associated species were contaminated with a small amount of dimethylmercury (identified by high resolution mass spectrometry) and attempts were made to synthesise absolutely pure dimethylmercury-free trimethylgallium. The gallium/dimethylmercury synthesis[176] always

Fig. 5 Metal Containing Ions Found in the Mass Spectra of Me_3M

$B^{216,217}$	Al^{132}	Ga	In	Tl
B	Al	Ga	In	Tl
BH	AlH	GaH	InH	TlH
BH_2	AlH_2	GaH_2	InH_2	TlH_2
		GaC	InC	TlC
BCH		GaCH	InCH	TlCH
BCH_2	$AlCH_2$	$GaCH_2$	$InCH_2$	$TlCH_2$
BCH_3	$AlCH_3$	$GaCH_3$	$InCH_3$	$TlCH_3$
BCH_4	$AlCH_4$	$GaCH_4$	$InCH_4$	$TlCH_4$
BC_2				
BC_2H				
BC_2H_2		GaC_2H_2		
BC_2H_3		GaC_2H_3		
BC_2H_4		GaC_2H_4		
BC_2H_5	AlC_2H_5	GaC_2H_5	InC_2H_5	TlC_2H_5
BC_2H_6	AlC_2H_6	GaC_2H_6	InC_2H_6	TlC_2H_6
			InC_2H_7	TlC_2H_7
BC_3H				
BC_3H_2				
BC_3H_3				
BC_3H_4				
BC_3H_5				
BC_3H_6		GaC_3H_6	InC_3H_6	TlC_3H_6
BC_3H_7				
BC_3H_8		GaC_3H_8	InC_3H_8	TlC_3H_8
BC_3H_9	AlC_3H_9	GaC_3H_9	InC_3H_9	TlC_3H_9
	Me_3Al_2	Me_3Ga_2		
	Me_5Al_2			
		$(Me_3Ga)_3$		

Fig. 6 Metal Containing Ions Found in the Mass Spectra of Trivinylgallium

Ga	GaC_3H_4
GaCH	GaC_3H_5
GaH_2	GaC_3H_6
	GaC_4H_2
GaC	GaC_4H_4
GaCH	GaC_4H_5
$GaCH_2$	GaC_4H_6
$GaCH_3$	GaC_4H_8
$GaCH_4$	GaC_4H_9
	GaC_5H_5
GaC_2	GaC_5H_8
GaC_2H	GaC_5H_9
GaC_2H_2	GaC_6H_8
GaC_2H_3	GaC_6H_9
GaC_2H_4	

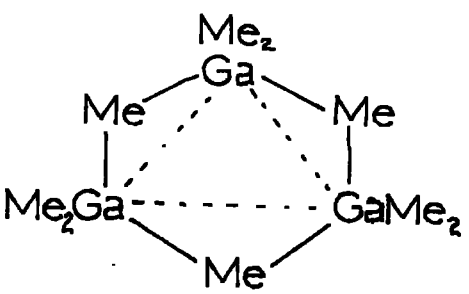


yielded, even after the most rigorous fractionation, trace amounts of dimethylmercury in the trimethylgallium. Interestingly no associated species were formed in the vapour phase of the samples made in Belfast.

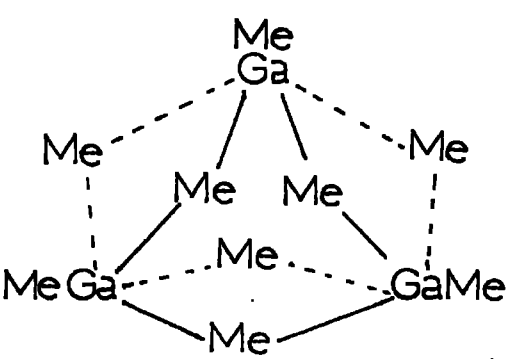
Trimethylgallium was also made by reacting aluminium trichloride with trimethylaluminium[86] and these samples also gave no associated species. The spectra were run with the source of the mass spectrometer freshly cleaned but this also gave no associated species from the samples made in Belfast. The history of the two samples which did give associated species was not particularly unusual in that they were stored on an all-glass vacuum line and exposed to no electromagnetic radiation other than ordinary sunlight (there being no evidence of photolytic instability[232]).

The n.m.r.[192] and Raman[232] spectra of trimethylgallium in dichloromethane show no evidence of association at -120° although recent work has shown that solid trimethylgallium is isomorphous with trimethylindium and trimethylthallium, presumably containing a similar tetrameric unit[232].

The existence of the species found is thus rather puzzling, especially with regard to their non-reproducibility in samples made in Belfast. The dimeric ion $Me_3Ga_2^+$ could be a fragment ion from a trimer rather than derived from a parent dimer ion $Me_6Ga_2^{+\cdot}$. Although no structural conclusions can be drawn on the basis of mass spectroscopic evidence alone, it is possible that the trimer molecule could involve methyl bridging groups either with or without (formulas 1 and 2) gallium-gallium interaction. In general the tendency towards metal-metal bonding increases in descending the periodic group.



1



2

Fig. 8a Variation of Ion Abundances with Source Temperature for $(Me_3Ga)_3$

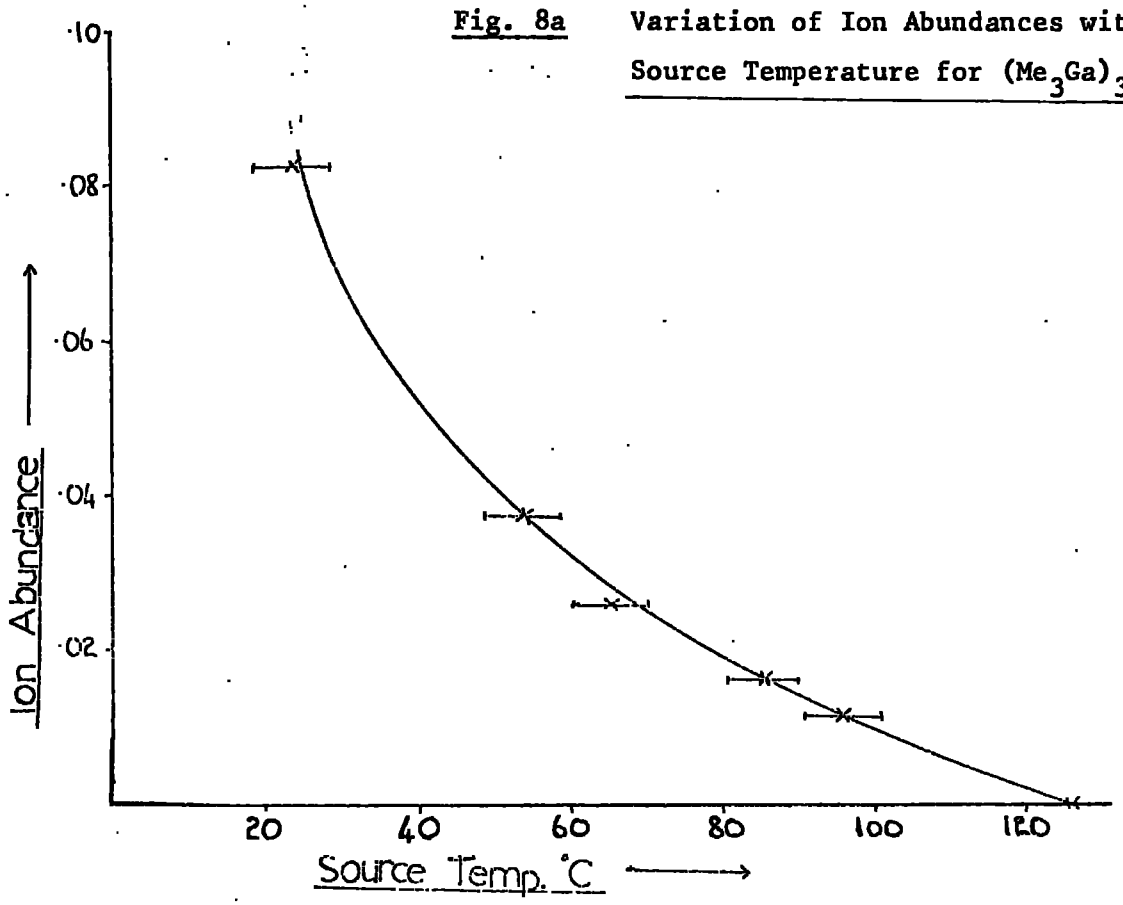
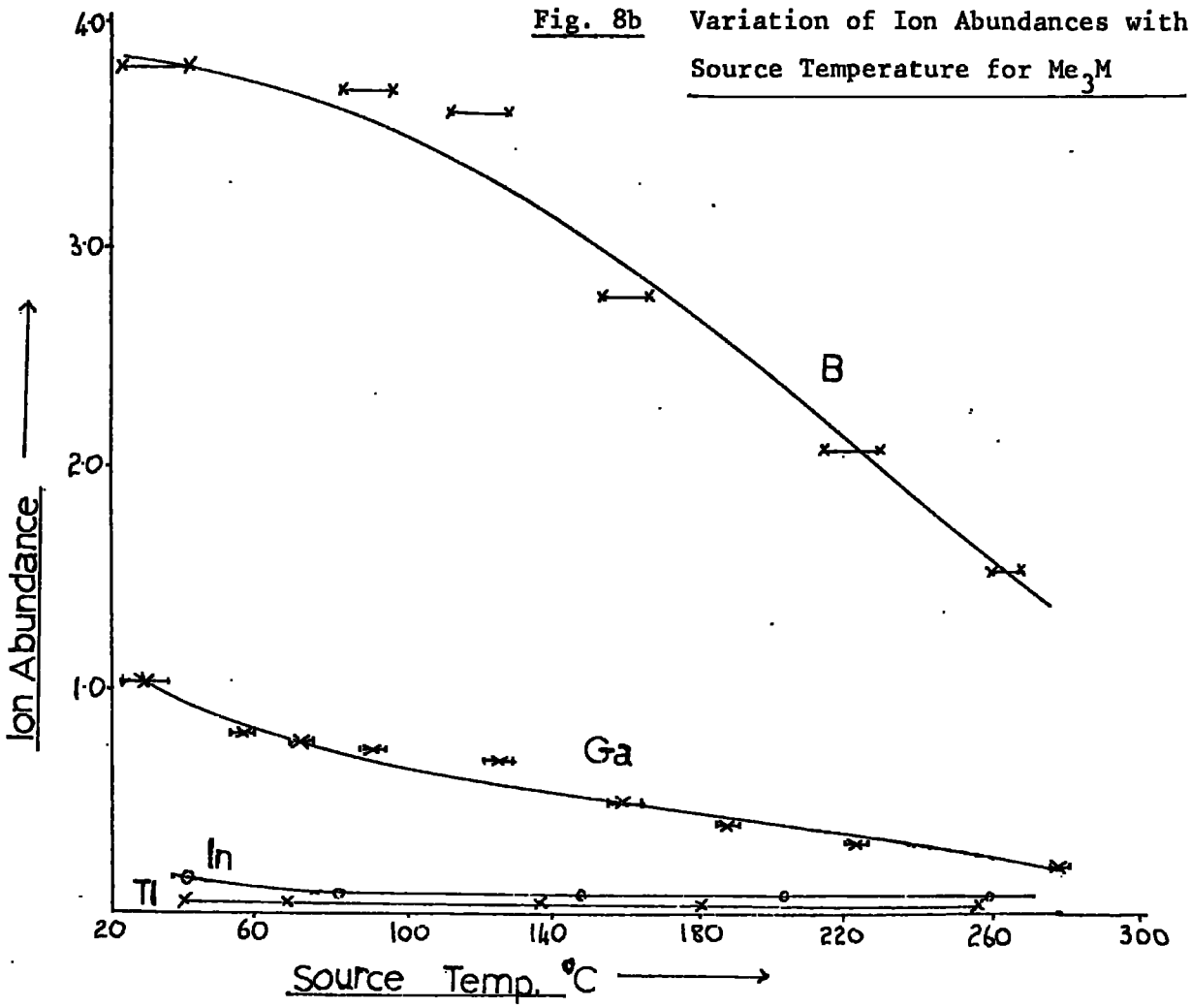


Fig. 8b Variation of Ion Abundances with Source Temperature for Me_3M



Essentially the mass spectrum confirms the observation that trimethylgallium is a monomer in the vapour phase. Trivinylgallium however has been shown to be a dimer in solution[182] although no investigation of the vapour phase association has been completed probably owing to the extreme instability of the compound even under vacuum. The mass spectrum of trivinylgallium showed no associated species but had low abundant fragment ions including $C_5H_9Ga^+$, $C_5H_8^+$ and $C_4H_4Ga^+$ which presumably must come from higher associated species which are decomposed under the conditions used.

The molecular ion $C_6H_9Ga^{+\cdot}$ is not apparent in the low resolution spectrum and is only seen under high resolution and so presumably as the monomer is so unstable within the mass spectrometer, it is not surprising that associated species are not seen.

Thus in the vapour phase the group III alkyls (other than Me_3Al) contain negligible amounts of associated species. This is in line with the theory that although molecular geometry can favour the formation of weakly bridged tetramers in the solid phase, in solution and in the vapour phase the compounds exist as monomers.

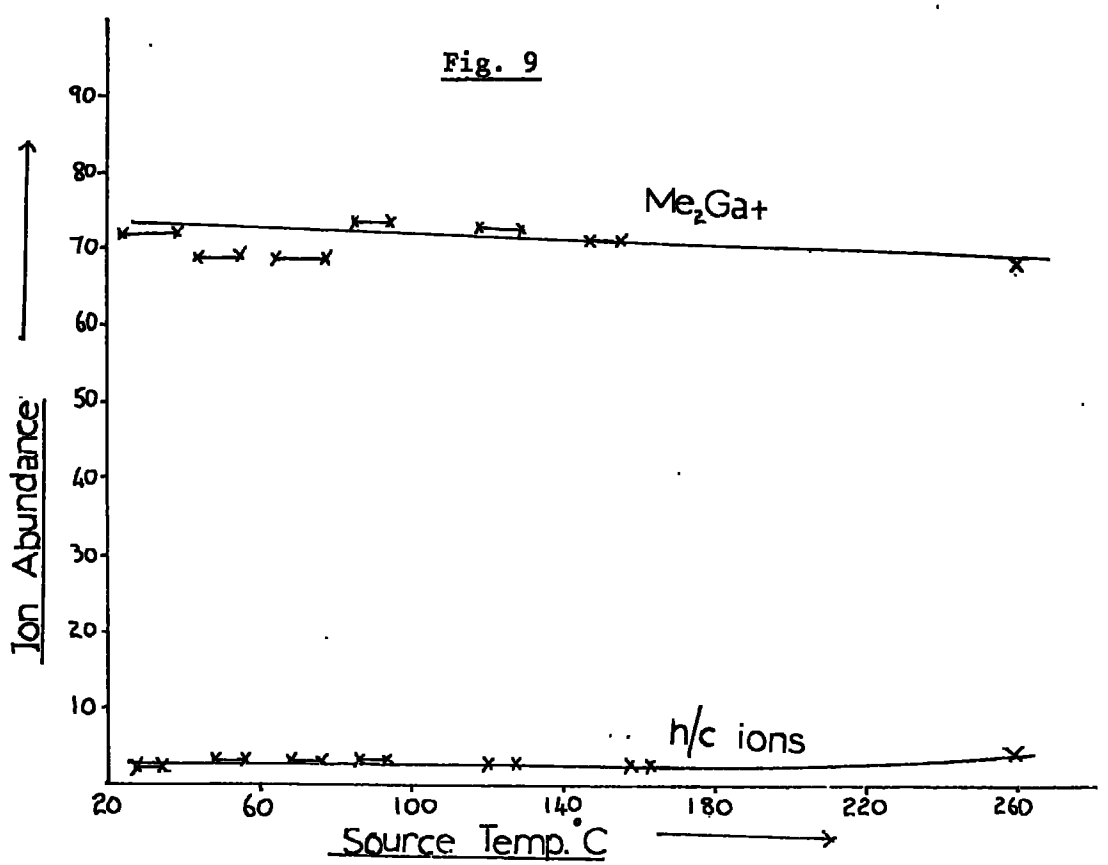
3.4.2 General Features of the Mass Spectra of the Group III Alkyls

The mass spectra of the group III alkyls have several salient comparative features which illustrate group trends, and will be discussed below.

(i) Abundance of the molecular ion

The abundances of the molecular ion of the series Me_3M is in the order Al>B>Ga>In>Tl. All molecular ions are of comparatively low abundance and decrease generally with increasing source temperature (see Fig. 8b). These points are a reflection on the decreasing M-C bond strength as the group is ascended and the decreasing stability of all of the alkyls as the temperature is raised. The molecular ion increased in relative

Fig. 9


Me2Ga+
h/c ions
Ion Abundance
Source Temp. °C
90
80
70
60
50
40
30
20
10
20
60
100
140
180
220
260

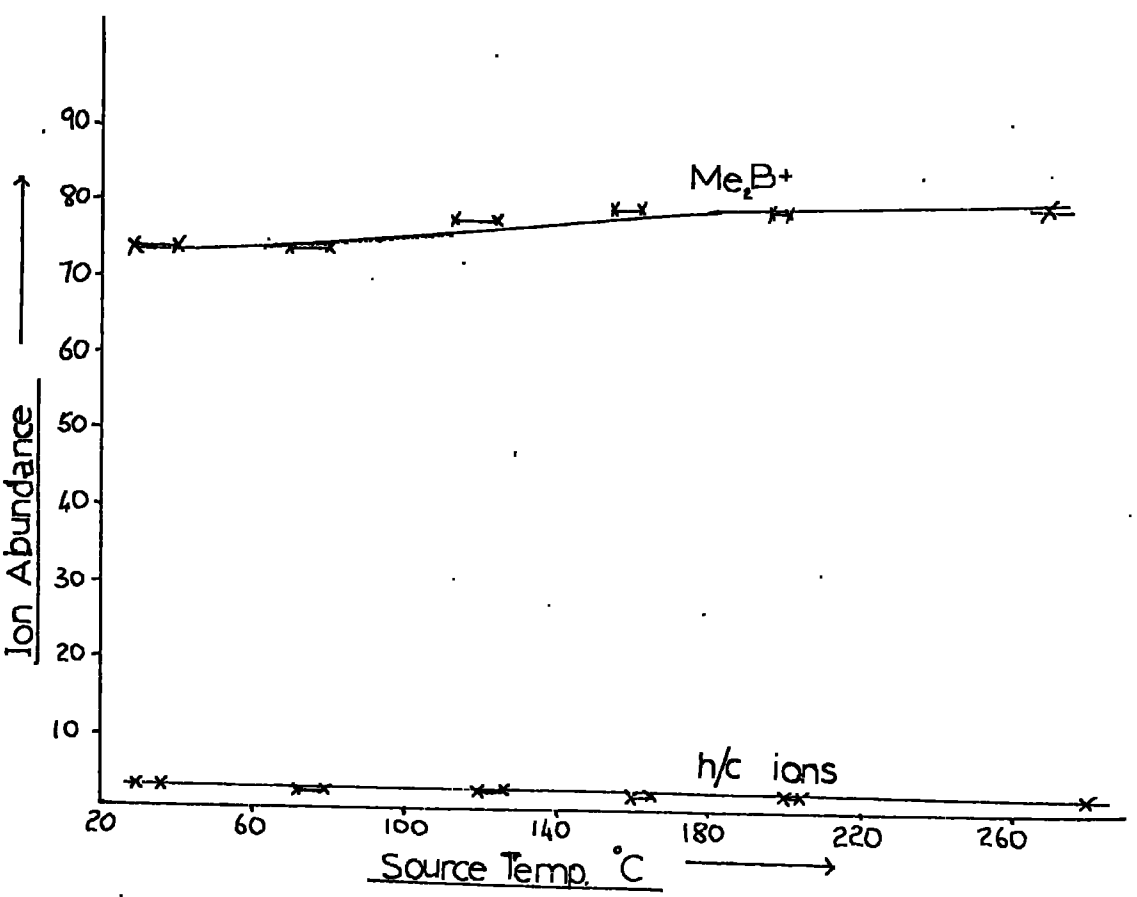
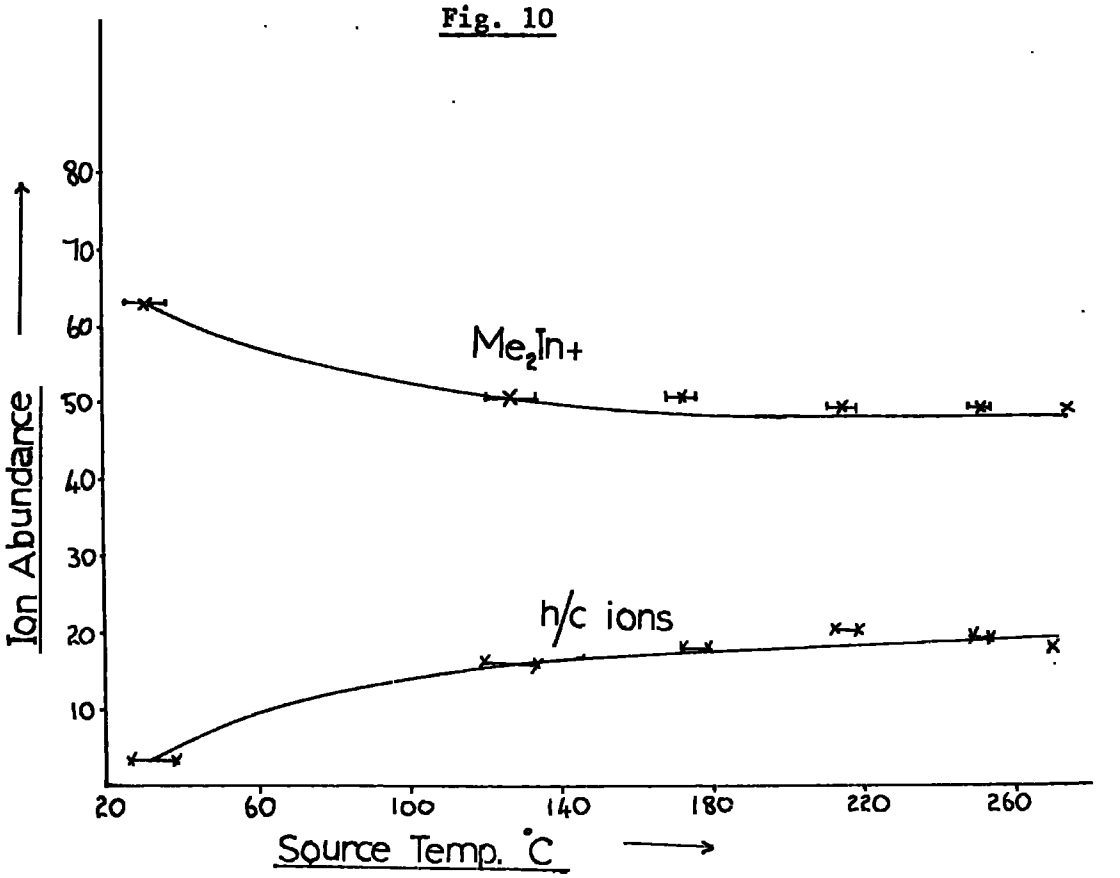

Me2B+
h/c ions
Ion Abundance
Source Temp. °C
90
80
70
60
50
40
30
20
10
20
60
100
140
180
220
260

Fig. 10


Ion Abundance
80
70
60
50
40
30
20
10
Me2In+
h/c ions
20
60
100
140
180
220
260
Source Temp. °C

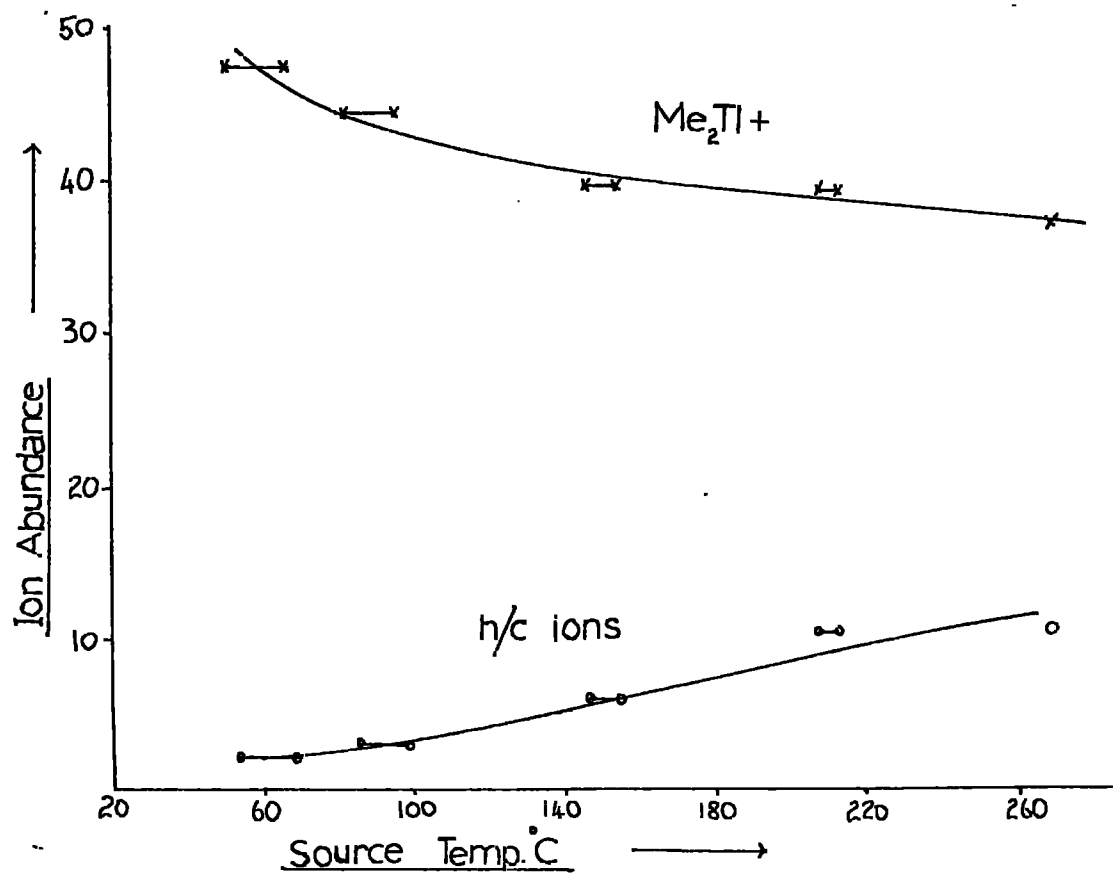
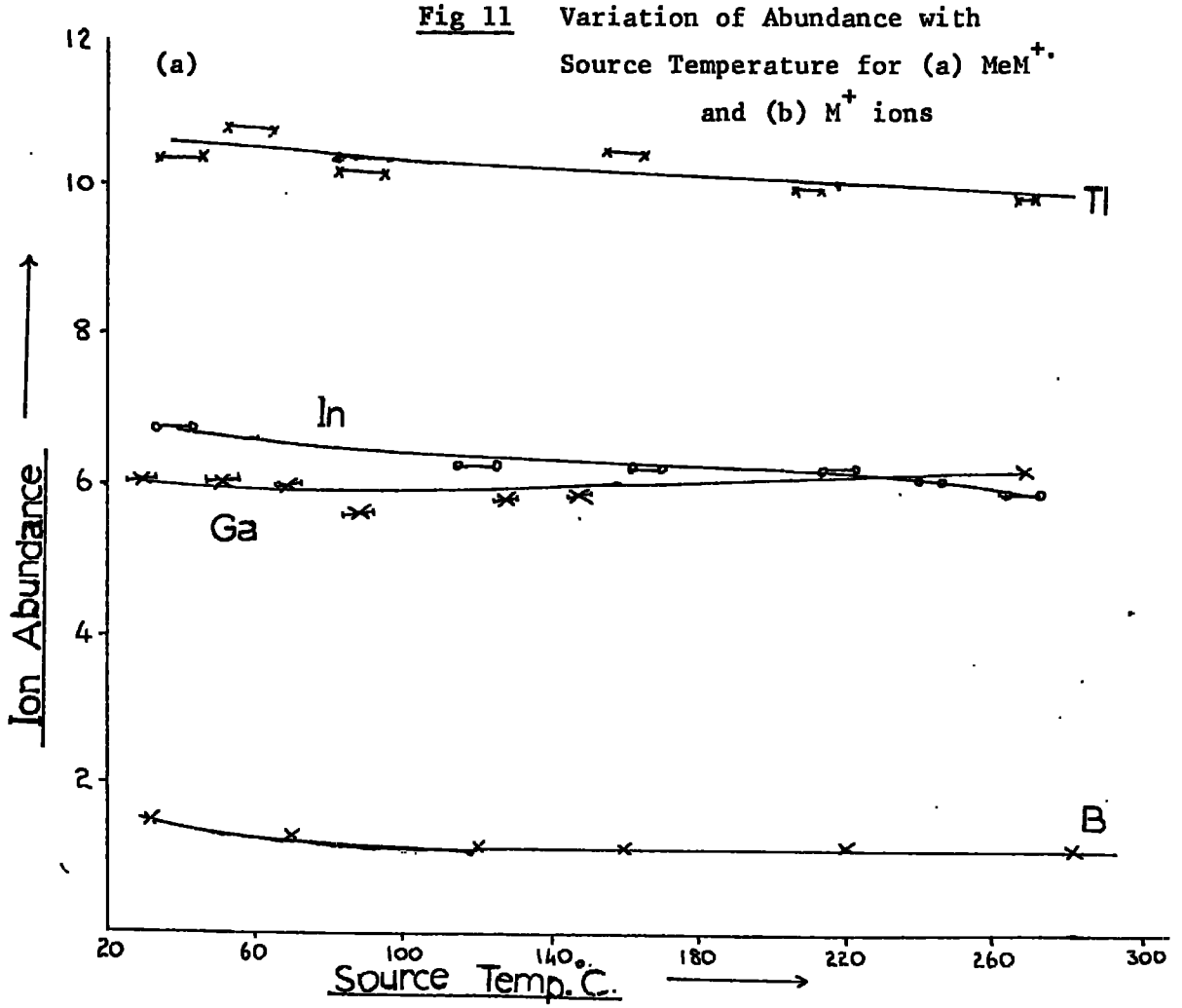
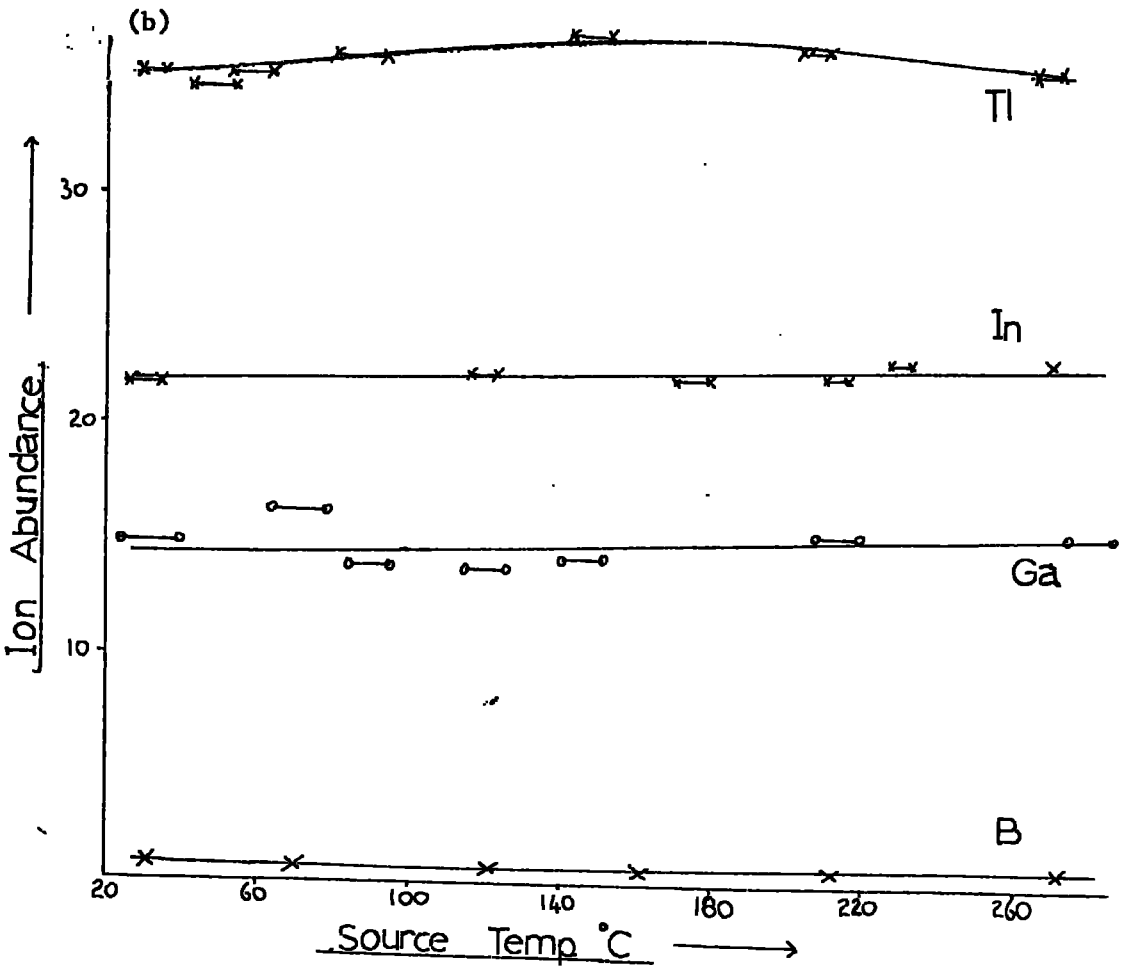

Ion Abundance
50
40
30
20
10
Me2Tl+
h/c ions
20
60
100
140
180
220
260
Source Temp. °C

Fig 11 Variation of Abundance with Source Temperature for (a) $MeM^{+\cdot}$ and (b) M^{+} ions





abundance as the ionising voltage was decreased and was present at all temperatures for all samples at 10eV.

(ii) The Me_2M^+ ion

This ion was the most abundant ion in all samples ranging from 75-79% abundance in Me_3B to 45-36% abundance in Me_3Tl. The variation in abundance with source temperature is interesting in that whereas Me_2B^+ tended to increase, Me_2Ga^+ remained fairly constant while Me_2In^+ and Me_2Tl^+ decreased in abundance as the source temperature was raised. (see Fig. 9 and 10). The decrease in abundance of Me_2In^+ and Me_2Tl^+ was matched by an increase in abundance of hydrocarbon ion m/e < 30 indicating probable decomposition of this species.

The Me_2M^+ ion is the most abundant ion at all temperatures and decreasing the ionising voltage to 10eV results in an increase in abundance of all Me_2M^+ species to 90-96% of the ion current.

(iii) The $MeM^{+\cdot}$ ion

This ion at low source temperatures varies in abundance from 1.3% for $MeB^{+\cdot}$ to 10% for $MeTl^{+\cdot}$ (see Fig. 11a). In general the abundance of the $MeM^{+\cdot}$ ion remains fairly constant or decreases slightly with increasing source temperature.

The higher abundance of the $MeM^{+\cdot}$ ion can be attributed to the increasing stability of the monovalent state as the group is ascended. The $MeM^{+\cdot}$ ions all decrease with lowering eV and have very low abundances at 10eV.

(iv) M^+ ion

The relative abundances of this ion (Fig. 11b) indicate the increasing metallic nature and lower ionising potential as the group is ascended. This is shown by the non-metallic boron with an M^+ ion abundance of 0.50%

to thallium which has an ion abundance of 36%. The ions increase in abundance B<(Al)<Ga<In<Tl. The abundances remain essentially constant with increasing source temperature and all decrease with decreasing ionising voltage.

(v) Hydrocarbon ion abundance (<30)

The variation of abundance with source temperature reflects generally the stability of the alkyls to heat. Trimethylboron is a comparatively stable compound decomposing at 400-600° and 1-6 atm. into methane, hydrogen and polymeric materials[233]. This is reflected in its mass spectrum[217] and the lack of variation of hydrocarbon ion abundance with source temperature. (Fig. 9a). Trimethylaluminium is pyrolysed at a lower temperature, 200-250°, [86] giving methane, aluminium carbide and polymeric material and this is reflected in the total hydrocarbon ion abundance in the mass spectrum which is little changed from source temperatures of 50-195°.[132] The hydrocarbon ion content in the mass spectrum of Me_3Ga shows a little variation with temperature over the temperature range 30-250°. (Fig. 9).

This is in line with the observation that Me_3Ga is a fairly stable compound being pyrolysed in toluene vapour at 410-510°.[140] The comparative instability of trimethylindium and trimethylthallium to heat is shown by the increase in hydrocarbon ion content as the source temperature is raised (Fig. 11).

This was expected since trimethylthallium for example is said to explode above 90° [86], although previous reports indicated that trimethylindium was stable at 250°.[196] All of the hydrocarbon ion abundances decrease with decreasing ionising voltage.

(vi) Other fragmentation ions

The abundances of these ions reflect the relative metal-carbon bond

strengths as the group is ascended. This is shown in the complex spectrum of trimethylboron which has many fragment ions of the type $C_xH_yB^+$ of medium abundance whereas the mass spectrum of trimethylthallium is relatively simple with only four or five major ions and fragment ions generally are of lower abundance. This is what one would expect as the B-C strength of about 80 kcal. $mole^{-1}$ is more comparable to the C-H bond strength than the Tl-C bond strength (27.4 kcal.$mole^{-1}$)[142]. Thus the higher the M-C bond strength, the greater the probability that C-H cleavage is as likely a process as M-C cleavage. This in turn implies a higher abundance of fragment ions.

Another point is that the abundance of MH_x^+ species decrease as the group is ascended possibly reflecting the instability of the hydrides of the higher members of the group.

3.4.3 Modes of Decomposition

In the limited number of compounds studied major ions are predominantly even-electron. The ratio of the abundances of the major even-electron to odd-electron metal-containing ions are shown in the table below.

Compound	Abundance of even-electron metal-containing ions (A)	Abundance of odd-electron metal-containing ions (B)	A/B
Me_3Al[132]	82.8	10.7	7.7
Me_3Ga	83.3	6.3	12.6
Me_3In	72.2	6.3	11.5
Me_3Tl	72.0	9.8	7.4

The modes of decomposition of the group III alkyls are similar to those of the group IV organo-compounds and may be classified in a similar way.

(a) Bond cleavage by radical elimination

With the exception of Me_3B, all the group III methyls produce a major even-electron ion by the loss of a methyl radical from the parent ion and/or a fragment ion.

(i) Me_3Ga

$$Me_3Ga^{+\cdot} \longrightarrow Me_2Ga^{+} + Me^{\cdot} \qquad m^* = 84.5,\ 86.0$$

$$Me_2Ga^{+} \longrightarrow MeGa^{+\cdot} + Me^{\cdot} \qquad m^* = 71.3,\ 73.2$$

$$MeGa^{+\cdot} \longrightarrow Ga^{+} + Me^{\cdot} \qquad m^* = 56.7,\ 58.6$$

(ii) Me_3In

$$MeIn^{+\cdot} \longrightarrow In^{+} + Me^{\cdot} \qquad m^* = 99.7,\ 101.7$$

(iii) Me_3Tl

$$MeTl^{+\cdot} \longrightarrow Tl^{+} + Me^{\cdot} \qquad m^* = 189,\ 191.$$

All of the metastables above are of medium to weak intensity and are not seen at 20eV at low source temperatures and in the case of thallium are not seen below 50eV at source temperatures above 150°. Presumably the absence of any metastables corresponding to loss of a methyl radical from the parent ion in Me_3Tl and Me_3In is due to the extremely low abundance of the parent ion.

The results in general are similar to those obtained with trimethyl aluminium[132].

(b) Rearrangement processes involving loss of a molecule

With all of the Me_3M compounds (except Me_3B) the elimination of ethane from the even-electron ion Me_2M^{+} is a major process, with strong metastable peaks. These were in all cases and all temperatures seen at 20eV.

$$Me_2Ga^+ \longrightarrow Ga^+ + C_2H_6 \qquad m^* = 49.9,\ 48.1$$

$$Me_2In^+ \longrightarrow In^+ + C_2H_6 \qquad m^* = 89.3,\ 91.20$$

$$Me_2Tl^+ \longrightarrow Tl^+ + C_2H_6 \qquad m^* = 191,\ 189$$

No metastable supported alkene or methane elimination was seen (unlike Me_3Al[132]) although hydrogen loss was confirmed in Me_3B as previous work has shown[217].

$$C_3H_6B^+ \longrightarrow C_2H_4B^+ + H_2 \qquad m^* = 37.1,\ 36.1$$

3.4.4 Appearance Potential Measurements

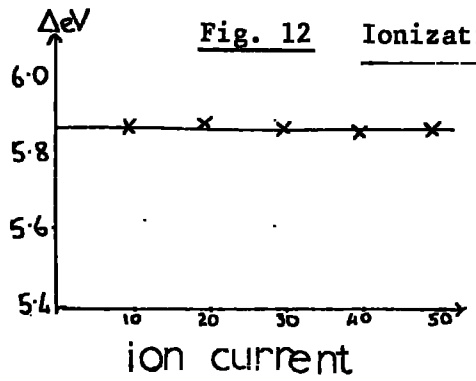
Appearance potential measurements were carried out on the major ions in the mass spectrum of trimethylgallium, using the Warren method described in section 3.2.5 of this thesis.

Ion	Appearance Potential eV	Value of individual determination	Standard	Source Temp.
$Me_3Ga^{+\cdot}$	9.87 ± 0.02	9.87, 9.85, 9.89	Ar	100
Me_2Ga^+	10.16 ± 0.03	10.13, 10.18, 10.17	Ar	100
$MeGa^{+\cdot}$	13.65 ± 0.07	13.58, 13.67, 13.72	Ar	100
Ga^+	13.24 ± 0.03	13.22, 13.24, 13.27	Ar	100

The ionisation efficiency curves are shown in Figs. 12 to 15. Using the relationships described in 3.1.13 of this thesis, the mean gallium-carbon bond energy in trimethylgallium is 55.6 ± 2 kcal.mole^{-1} and in the molecular ion $Me_3Ga^{+\cdot}$ the mean gallium-carbon bond strength is 25.90 ± 2 kcal.mole^{-1}.

The former is in close agreement with the value 56.7 ± 2 kcal.mole^{-1} obtained using calorimetric methods[138].

Fig. 12 Ionization Efficiency Curve for $Me_3Ga^{+\cdot}$ and $Ar^{+\cdot}$



$I(Me_3Ga^{+\cdot}) = I(Ar) - 5.90$

$= 15.77 - 5.90$

$= 9.87$ eV

Me_3Ga^{+}

$Ar^{+\cdot}$

ΔV

Ion Current

10^4

10^3

10^2

10

1

8 10 12 14 16 18 20

Electron Energy eV

Fig. 13 Ionization Efficiency Curve for Me_2Ga^+ and $Ar^{+\cdot}$

$I(Me_2Ga^+) = I(Ar) - 5.64$

$= 15.77 - 5.64$

$= \underline{10.13 eV}$

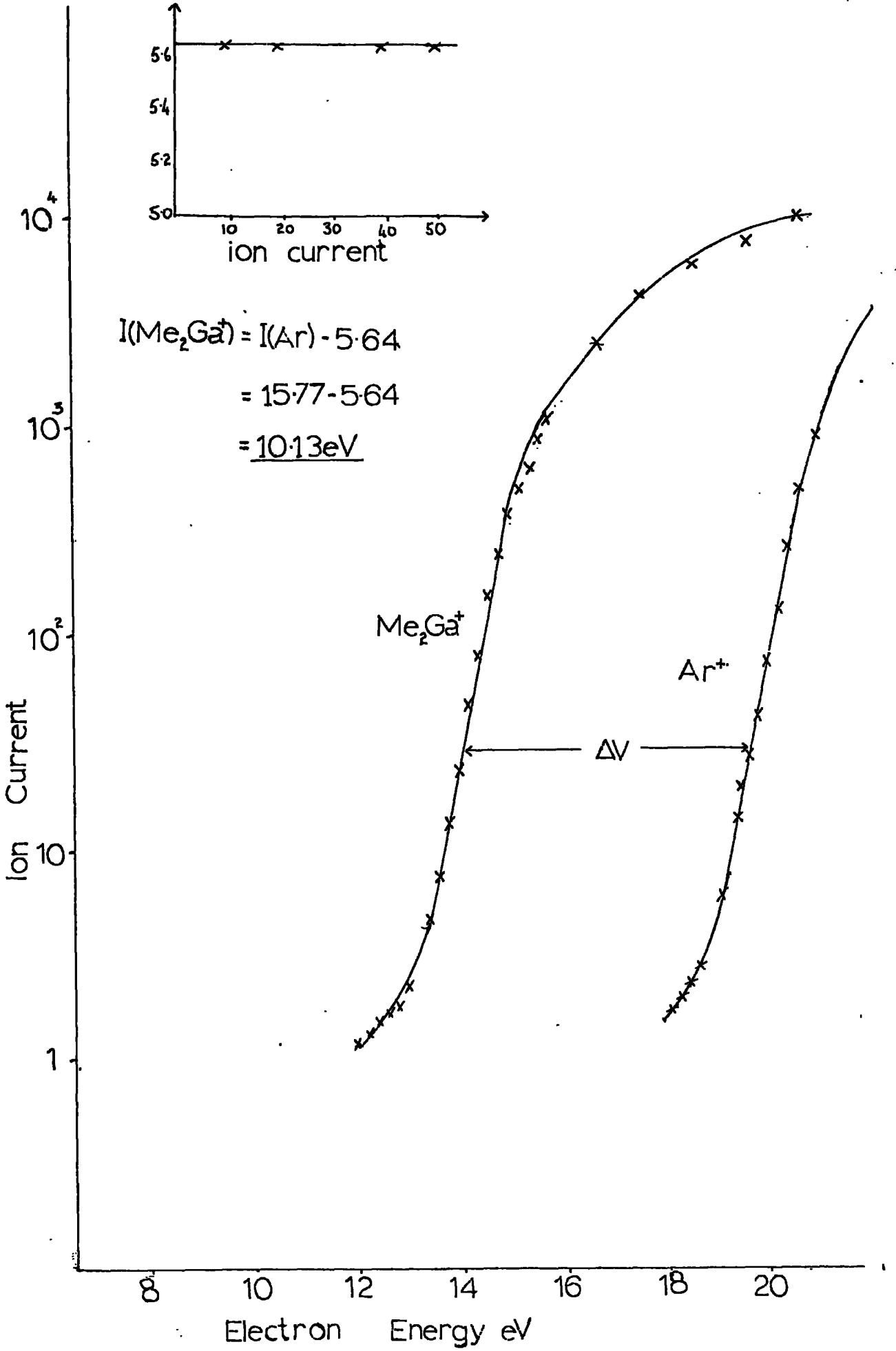
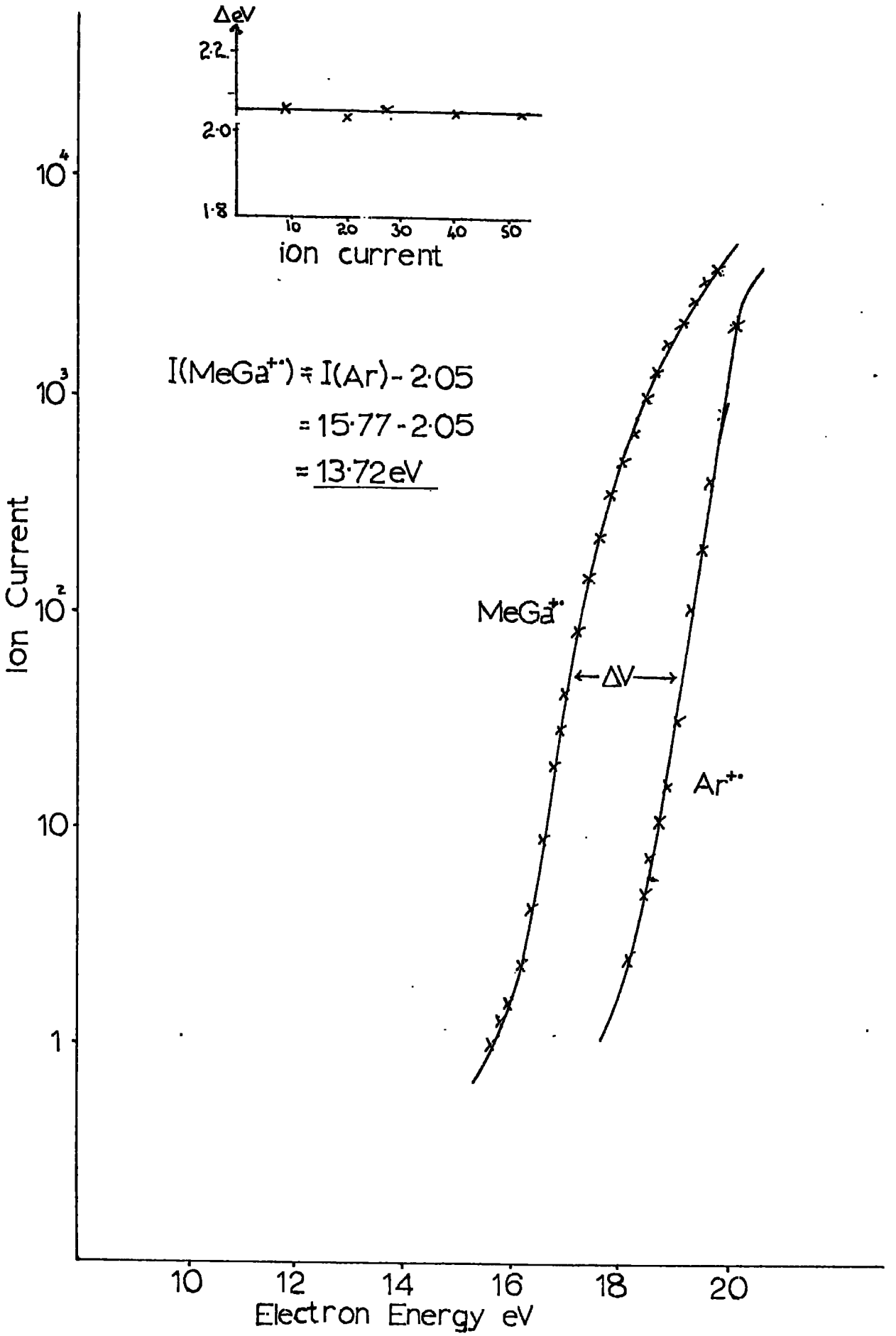


Fig. 14 Ionization Efficiency Curve for $MeGa^{+\cdot}$ and $Ar^{+\cdot}$



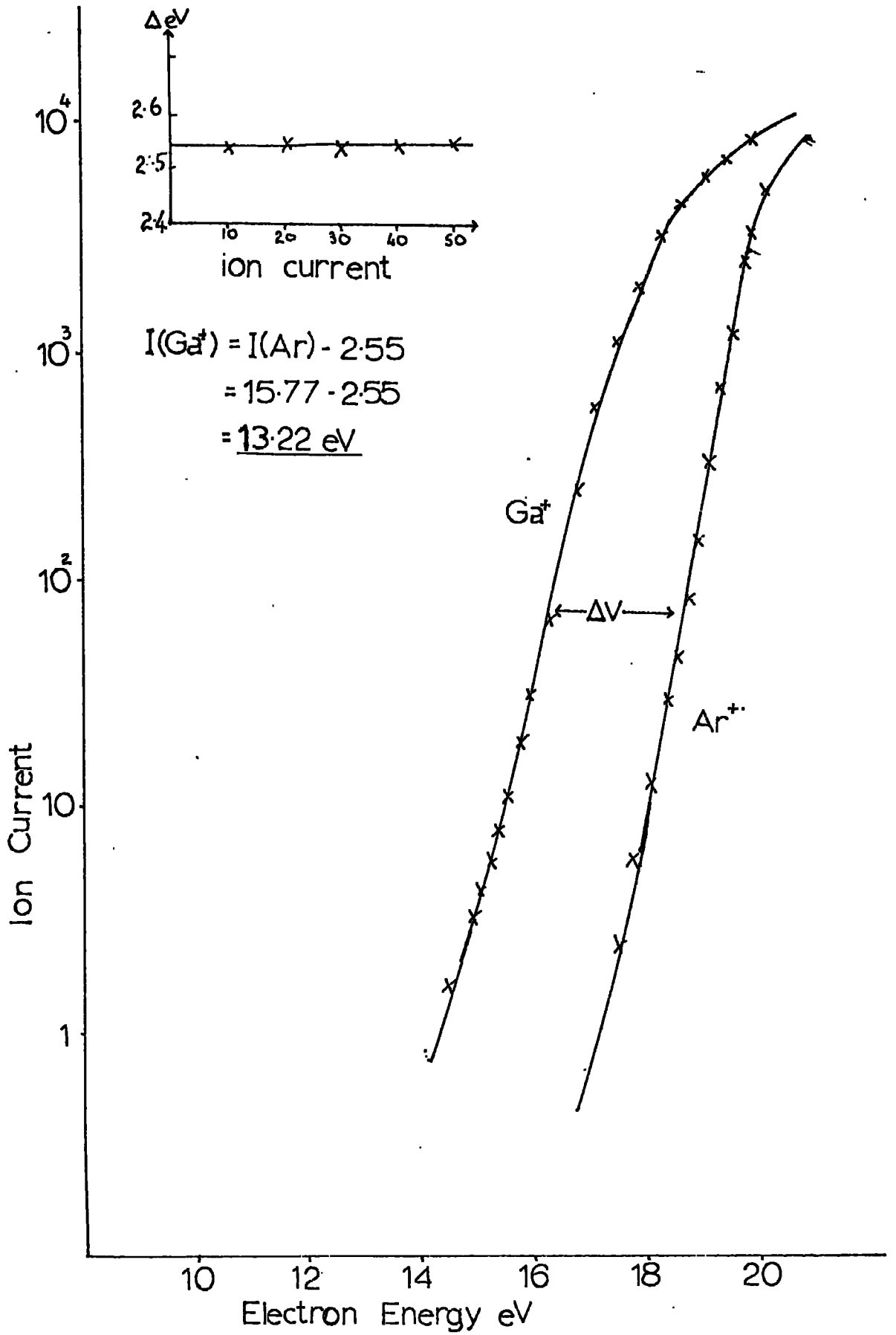


Fig. 15 Ionization Efficiency Curve for Ga^+ and $Ar^{+\cdot}$

The appearance potentials listed above are interesting in that they preclude a simple threshold dissociation process:

$$Me_3Ga^{+\cdot} \xrightarrow{-Me\cdot} Me_2Ga^{+} \xrightarrow{-Me\cdot} MeGa^{+\cdot} \xrightarrow{-Me\cdot} Ga^{+}$$

as $A(Ga^+)$ is smaller than $A(MeGa^{+\cdot})$. Presumably a large proportion of the gallium ions are formed from the process.

$$Me_2Ga^{+} \longrightarrow Ga^{+} + C_2H_6 \qquad m^* = 48,\ 50$$

The metastable peaks for this transition are extremely large confirming that it is in fact a major process.

3.4.5 The Mass Spectrum of Trivinylgallium

The variation of abundances with source temperature of the major ions in the mass spectrum of trivinylgallium are shown below and in Fig. 16.

Metal-Containing Ions

Source Temp.	$(Vi)_3Ga$	$(Vi)_2Ga$	C_2H_4Ga	ViGa	Ga
30-50	0.05	37.6	8.8	15.2	23.8
95-105	0.04	38.5	8.8	13.1	23.4
145-155	0.03	40.5	9.1	13.9	21.1
200-205	0.01	39.0	10.6	11.4	20.9
250	0.01	37.3	7.8	10.7	14.2

Hydrocarbon Ions

Source Temp.	C_4H_x	C_3H_x	C_2H_x	CH_x
30-50	2.3	2.8	5.6	0.2
95-105	3.0	3.2	5.6	0.2
145-155	3.0	3.2	5.2	0.1
200-205	3.2	4.2	6.7	0.2
250	4.8	4.8	8.7	0.3

Although generally the spectrum resembles that of trimethylgallium there are important differences. The molecular ion is of extremely small abundance and this together with the absence of any associated species reflect the instability of the compound in the mass spectrometer. The lower abundance of the dialkyl species (relative to Me_2Ga^+) coupled with higher abundances of the metal ion and the monoalkyl species $C_2H_4Ga^+$ and $C_2H_3Ga^{+\cdot}$ reflect the lower stability of the divinyl-moiety and its susceptibility to radical and alkene loss. A further feature in which the mass spectrum of trivinylgallium differs from that of trimethylgallium is the high abundance of hydrocarbon ions and the presence of many low-abundant fragment gallium-containing ions. (see Fig. 6).

As would be expected the abundance of all metal-containing ions fell as the source temperature increased with a corresponding rise in abundance of hydrocarbon ions.

The ratio of even-electron to odd-electron metal-containing ions is seen below.

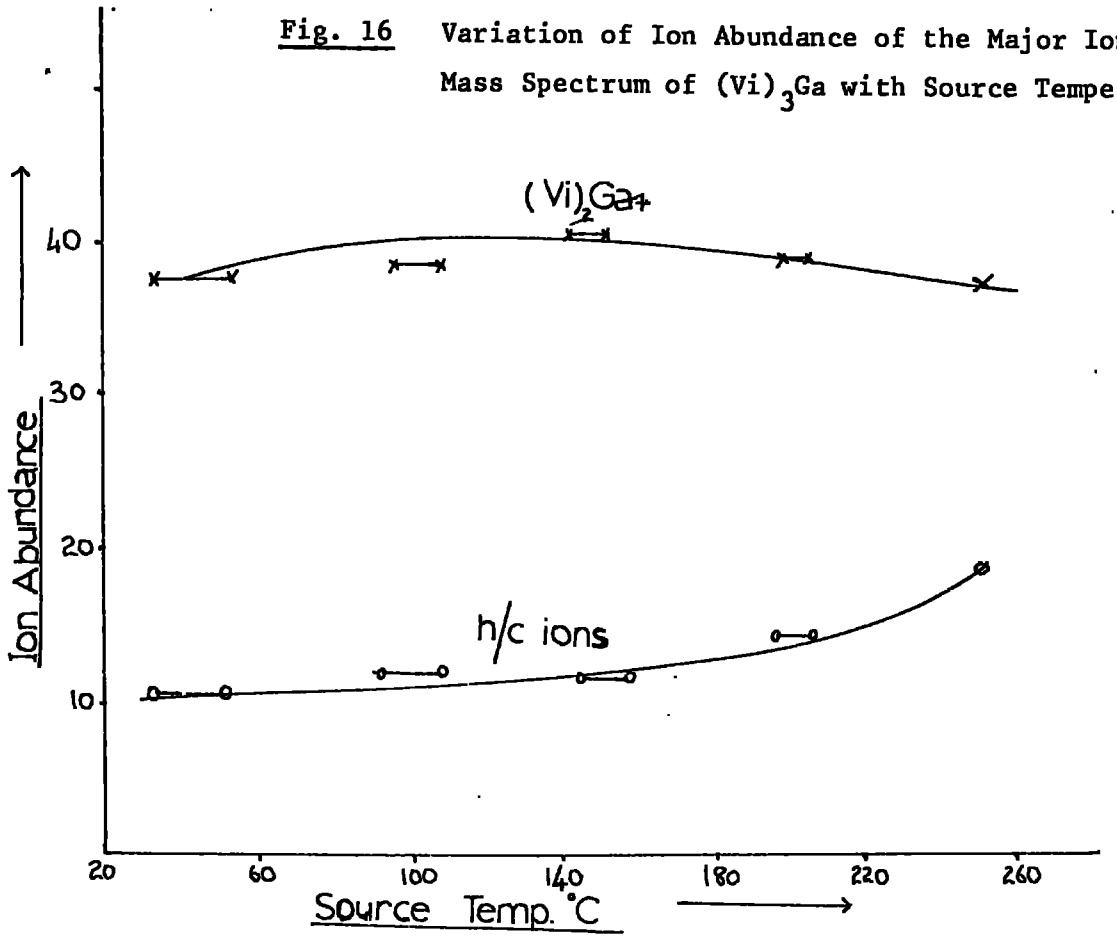
Source Temp.	Even-electron Abundance	Odd-electron Abundance	Ratio
30-50	70.3	15.2	4.6
95-105	70.8	13.1	5.4
145-155	70.9	13.9	5.1
200-205	70.5	11.4	6.2
250	64.5	10.7	6.0

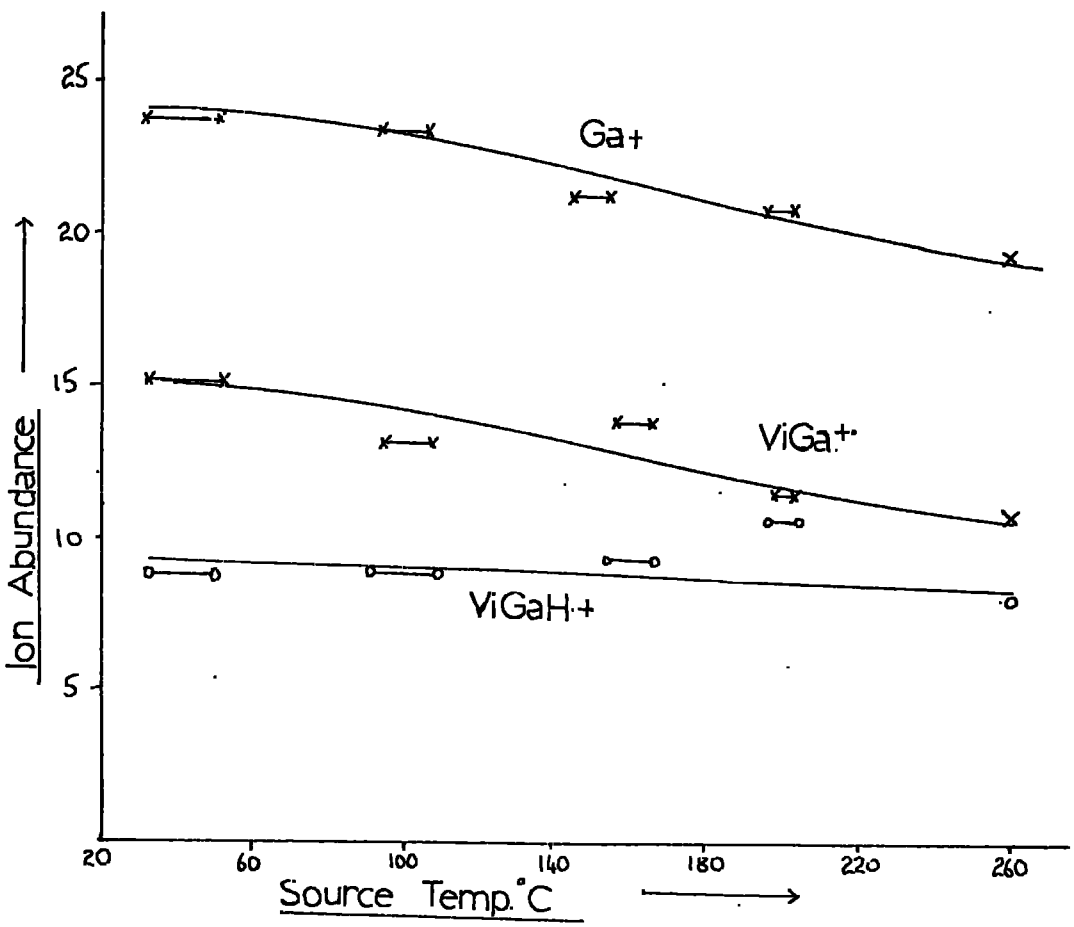
The corresponding ratio for Me_3Ga is 12.6. This reflects the greater proportion of odd-electron metal-containing ions in the spectrum of trivinylgallium and possibly the difference in decomposition modes.

A major process is the loss of butadiene from the $(Vi)_2Ga^+$ ion.

$$(Vi)_2Ga^+ \longrightarrow C_4H_6 + Ga^+ \qquad m^* = 38.7,\ 40.2$$

Fig. 16 Variation of Ion Abundance of the Major Ions in the Mass Spectrum of $(Vi)_3Ga$ with Source Temperature





The butadiene is in such high abundance that it itself undergoes at least one metastable-supported decomposition.

$$C_4H_8^{+\cdot} \longrightarrow CH_3\cdot + C_3H_3^{+} \qquad m^* = 28.2$$

Another major process is the loss of acetylene from the $(Vi)_2Ga^+$ ion.

$$(Vi)_2Ga^+ \longrightarrow C_2H_2 + ViGaH^+ \qquad m^* = 76.4,\ 78.3$$

This is a high energy process and the abundance of the $ViGaH^+$ decreases considerably below 20eV. The $ViGaH^+$ ion then undergoes ethylene elimination forming the Ga^+ ion.

$$ViGaH^+ \longrightarrow Ga^+ + C_2H_4 \qquad m^* = 49.08,\ 50.9$$

Metastable peaks corresponding to the transitions:

$$(Vi)_3Ga^{+\cdot} \xrightarrow{-Vi\cdot} (Vi)_2Ga^+ \xrightarrow{-Vi\cdot} ViGa^{+\cdot} \xrightarrow{-Vi\cdot} Ga^+$$

were not observed and presumably is not a major process. This is an important difference between the decomposition modes of trimethyl- and trivinylgallium.

The high abundance of hydrocarbon ion in the spectrum meant that several metastable transition involving purely hydrocarbon species were also seen.

Variation of the eV rather surprisingly did not alter the spectrum very much in that very few ions disappeared. All ions except $(Vi)_2Ga^+$ and $(Vi)_3Ga^{+\cdot}$ generally decreased in abundance below 20eV but all major ions (including $(Vi)_3Ga^{+\cdot}$) were present at 10eV at all temperatures.

APPENDIX 1

Accurate masses for trimethylgallium, trimethylindium and trimethyl thallium using triperfluorobutylamine as reference standard.

Table A1 : 1

Accurate Masses of Metal-Containing Ions in the Mass Spectrum of Trimethylgallium

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
69	^{69}Ga	68.925682	68.925664	1
70	^{69}GaH	69.933590	69.933659	1
71	$^{69}GaH_2$	70.941560	70.941601	1
	^{71}Ga	70.924840	70.924454	5
72	^{71}GaH	71.932810	71.932819	1
73	$^{71}GaH_2$	72.940780	72.940839	1
81	$^{69}Ga^{12}C$	80.925682	80.925924	3
82	$^{69}Ga^{12}CH$	81.933652	81.933701	1
83	$^{69}Ga^{12}CH_2$	82.941201	82.941281	1
	$^{71}Ga^{12}C$	82.924840	82.924596	3
84	$^{69}Ga^{12}CH_3$	83.949592	83.949267	3
	$^{71}Ga^{12}CH$	83.932810	83.932744	1
85	$^{69}Ga^{12}CH_4$	84.957562	84.957171	5
	$^{71}Ga^{12}CH_2$	84.940359	84.940729	4
86	$^{71}Ga^{12}CH_3$	85.948750	85.948391	4
87	$^{71}Ga^{12}CH_4$	86.956720	86.95706	4
95	$^{69}Ga^{12}C_2H_2$	94.941622	94.941599	1
96	$^{69}Ga^{12}C_2H_3$	95.949592	95.949574	1
97	$^{69}Ga^{12}C_2H_4$	96.957562	96.957549	1
	$^{71}Ga^{12}C_2H_2$	96.940780	96.940717	1

Table A1 : 1 (contd.)

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
98	$^{69}Ga^{12}C_2H_5$	97.965532	97.964967	6
	$^{71}GaC_2H_3$	97.948750	97.948692	1
99	$^{69}Ga^{12}C_2H_6$	98.973502	98.972942	6
	$^{71}Ga^{12}C_2H_4$	98.956720	98.956818	1
100	$^{71}Ga^{12}C_2H_5$	99.964690	99.965188	5
	$^{69}Ga^{12}C^{13}CH_6$	99.976852	99.976114	6
101	$^{71}Ga^{12}C_2H_6$	100.972660	100.973062	5
102	$^{71}Ga^{12}C^{13}CH_6$	101.976010	101.975483	5
111	$^{69}Ga^{12}C_3H_6$	110.973502	110.973052	4
113	$^{69}Ga^{12}C_3H_8$	112.989442	112.989113	3
	$^{71}Ga^{12}C_3H_6$	112.972660	112.973112	4
114	$^{69}Ga^{12}C_3H_9$	113.997412	113.996395	8
115	$^{71}Ga^{12}C_3H_8$	114.988600	114.988590	1
116	$^{71}Ga^{12}C_3H_9$	115.996570	115.997140	5
183	$^{138}Ga_2{}^{12}C_3H_9$	182.923094	182.923047	1
185	$^{140}Ga_2{}^{12}C_3H_9$	184.922252	184.922436	1
187	$^{142}Ga_2{}^{12}C_3H_9$	186.921410		
342	$^{207}Ga_3{}^{12}C_9H_{27}$	341.992236	341.994629	7
344	$^{209}Ga_3{}^{12}C_9H_{27}$	343.991394	343.991250	1
346	$^{211}Ga_3{}^{12}C_9H_{27}$	345.990552	345.987902	8
348	$^{213}Ga_3{}^{12}C_9H_{27}$	347.989710	347.989443	1

Table A1 : 2

Accurate Masses of Metal-Containing Ions in the Mass Spectrum of Trimethylindium

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
113	^{113}In	112.904280	112.904180	1
114	^{113}InH*	113.912250		
115	$^{113}InH_2$*	114.920220		
	^{115}In	114.904070	114.903979	1
116	^{115}InH	115.912040	115.911938	1
117	$^{115}InH_2$	116.920010	116.919896	1
125	$^{113}In^{12}C$	124.904280	124.904456	2
126	$^{113}In^{12}CH$	125.912250	125.912541	3
127	$^{113}In^{12}CH_2$	126.920220	126.920518	3
	$^{115}In^{12}C$	126.904070	126.904502	3
128	$^{113}In^{12}CH_3$	127.928190	127.928428	2
	$^{115}In^{12}CH$	127.912040	127.912365	3
129	$^{113}In^{12}CH_4$	128.936160	128.936372	2
	$^{115}In^{12}CH_2$	128.920010	128.920346	2
130	$^{115}In^{12}CH_3$	129.927980	129.928208	2
131	$^{115}In^{12}CH_4$	130.935950	130.936189	2
142	$^{113}In^{12}C_2H_5$	141.944130	141.944485	3
143	$^{113}In^{12}C_2H_6$	142.952100	142.950925	8
144	$^{113}In^{12}C_2H_7$	143.960070	143.960789	5
	$^{115}In^{12}C_2H_5$	143.943920	143.943190	5

Table A1 : 2 (contd.)

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
145	$^{115}In^{12}C_2H_6$	144.951890	144.950730	8
146	$^{115}In^{12}C_2H_7$	145.95986	145.958502	8
155	$^{113}In^{12}C_3H_6$*	154.952100		
157	$^{115}In^{12}C_3H_6$	156.951890	156.951764	1
	$^{113}In^{12}C_3H_8$*	156.968040		
158	$^{113}In^{12}C_3H_9$*	157.976010		
159	$^{115}In^{12}C_3H_8$	158.967830	158.967036	5
160	$^{115}In^{12}C_3H_9$	159.975800	159.975121	4

*Abundances too low for accurate mass measurement.

Table A1 : 3

Accurate Masses of Metal-Containing Ions in the Mass Spectrum of Trimethylthallium

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
203	^{203}Tl	202.972331	202.973169	4
204	^{203}TlH	203.980301	203.980192[a]	1
205	$^{203}TlH_2$	204.988271*		
	^{205}Tl	204.974462	204.975268[a]	4
206	$^{203}TlH_3$	205.996241	205.996200[a]	1
	^{205}TlH	205.982432	205.982229	1
207	$^{205}TlH_2$	206.990402	206.990397[a]	1
208	$^{205}TlH_3$	207.998372	207.998300[a]	1
215	$^{203}Tl^{12}C$	214.972331	214.973361	5
216	$^{203}Tl^{12}CH$	215.980301	215.981041	3
217	$^{203}Tl^{12}CH_2$	216.988271	216.988293	1
	^{205}TlC	216.974462	217.973314	5
218	$^{203}Tl^{12}CH_3$	217.996241	217.996188	1
	$^{205}Tl^{12}CH$	217.982432	217. 982710	2
219	$^{203}Tl^{12}CH_4$	219.004211	219.004625	1
	$^{205}Tl^{12}CH_2$	218.990402	218.990495	1
220	$^{205}Tl^{12}CH_3$	219.998372	219.997990	2
221	$^{205}Tl^{12}CH_4$	221.006342	221.004448	8
232	$^{203}Tl^{12}C_2H_5$	232.012181	232.013074	4

Table A1 : 3 (contd.)

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
233	$^{203}Tl^{12}C_2H_6$	233.020151	233.020846	3
234	$^{203}Tl^{12}C_2H_7$	234.028121	234.028823	3
	$^{203}Tl^{13}C^{12}CH_6$	234.023501*		
	$^{205}Tl^{12}C_2H_5$	234.014312	234.015917	6
235	$^{205}Tl^{12}C_2H_6$	235.022282	235.023469	5
236	$^{205}Tl^{12}C_2H_7$	236.030252	236.029489	3
	$^{205}Tl^{12}C^{13}CH_6$	236.025632*		
245	$^{203}Tl^{12}C_3H_6$	245.020151*		
247	$^{203}Tl^{12}C_3H_8$	247.036091	247.036810	3
	$^{205}Tl^{12}C_3H_6$	247.022282	247.022951	3
248	$^{203}Tl^{12}C_3H_9$	248.044061	248.045053	4
249	$^{205}Tl^{12}C_3H_8$	249.038222	249.038969	3
250	$^{205}Tl^{12}C_3H_9$	250.046192	250.045167	4

*Abundances too low for accurate mass measurement.

[a]These ions were of extremely low abundance.

APPENDIX 2

Ion abundances, as percentage of total ion current, for trimethylboron, trimethylgallium, trimethylindium and trimethylthallium at 70, 50, 20, 12 and 10 eV and high and low source temperatures.

Table A2 : 1

Ion Abundances of Me_3B Source Temperature 30-50°

Ion*	70	50	20	12	10
BC_3H_9	3.90	3.89	2.72	7.06	9.53
BC_3H_8	1.02	1.65	0.05		
BC_3H_7	0.57	0.50	0.41	0.11	
BC_3H_6	0.48	0.53	0.03		
BC_3H_5	0.09	0.04			
BC_3H_4	0.43	0.53			
BC_3H_3	0.64	0.71			
BC_3H_2	0.42	0.52			
BC_3H	0.14	0.09			
BC_3	0.08	0.07			
BC_2H_6	74.2	74.54	88.40	91.1	89.57
BC_2H_5	2.68	5.00	1.62		
BC_2H_4	5.0	3.20	3.54	0.73	
BC_2H_3	0.51	0.78			
BC_2H_2	2.32	3.68	0.39		
BC_2H	0.43	0.23			
BC_2	0.01	0.02			
C_2H_6	0.83	0.80	0.25		
C_2H_5	0.33	0.24	0.24	0.14	0.14
C_2H_4	0.26	0.27	0.24	0.25	0.19

Table A2 : 1 (contd.)

Ion*	70	50	20	12	10
C_2H_3 / BCH_4	2.15	2.78	1.3	0.09	
C_2H_2 / BCH_3	1.64	1.15	0.30	0.09	0.14
C_2H / BCH_2	0.17	0.24			
C_2 / BCH	0.08	0.07			
CH_4	0.07	0.05	0.05		
CH_3	0.57	0.66	0.20		0.14
CH_2	0.20	0.20			
BH_2 / CH	0.26	0.33	0.07		
C / BH	0.1	0.09			
B	0.63	0.53			

*Corrected to monoisotopic.

Table A2 ; 2

Ion Abundances of Me_3B Source Temperature 160-170°

Ion*	70eV	50eV	20eV	12eV	10eV
BC_3H_9	2.72	2.66	3.55	4.82	6.23
BC_3H_8	0.67	0.67			
BC_3H_7	0.34	0.12	0.03	0.02	
BC_3H_6	0.62	0.68	0.06	0.11	
BC_3H_5	0.05	0.05	0.05		
BC_3H_4	0.47	0.56	0.02		
BC_3H_3	0.70	0.70			
BC_3H_2	0.71	0.46	0.01		
BC_3H	0.19	0.09	0.01		
BC_3	0.04	0.03	0.02	0.02	
BC_2H_6	78.9	79.62	89.34	94.47	93.55
BC_2H_5	0.49	0.49	3.6		
BC_2H_4	4.71	5.01	2.22	0.12	
BC_2H_3	0.20	0.70	0.11		
BC_2H_2	2.57	2.57	1.97		
BC_2H	0.34	0.29	0.11	0.06	
BC_2	0.07	0.04			
C_2H_6	0.32	0.29	0.10	0.03	
C_2H_5	0.12	0.11	0.10	0.04	0.02
C_2H_4	0.23	0.22	0.10	0.08	0.08

Table A2 : 2 (contd.)

Ion*	70ev	50eV	20eV	12eV	10eV
BH_4 / C_2H_3	2.17	2.46	0.86	0.05	
B_3CH_3 / C_2H_2	1.23	1.23	0.31	0.04	0.04
BCH_2 / C_2H	0.01	0.01			
BCH / C_2	0.07	0.04			
CH_4	0.08	0.74	0.06	0.04	
CH_3	0.39	0.39	0.11	0.08	0.06
CH_2	0.12	0.10	0.01		
CH / BH_2	0.31	0.30	0.04		
C / BH	0.08	0.08	0.02		
B	0.45	0.38			

*Corrected to monoisotopic.

Table A2 : 3

Ion Abundances of Me_3B Source Temperature 270°

Ion*	70eV	50eV	20eV	12eV	10eV
BC_3H_9	1.46	1.76	2.18	4.13	5.07
BC_3H_8	0.62	0.61			
BC_3H_7	0.16	0.11	0.03		
BC_3H_6	0.58	0.68	0.62	0.12	
BC_3H_5	0.05	0.06	0.01		
BC_3H_4	0.48	0.57	0.03		
BC_3H_3	0.75	0.74	0.03	0.05	
BC_3H_2	0.85	0.39	0.01		
BC_3H	0.06	0.13	0.01		
BC_3	0.06	0.03	0.03		
BC_2H_6	79.1	77.6	91.0	95.1	94.8
BC_2H_5	0.65	0.61			
BC_2H_4	4.19	5.44	3.24	0.16	
BC_2H_3	0.01	0.10			
BC_2H_2	4.03	2.48	0.42		
BC_2H	0.24	0.42		0.09	
BC_2	0.08	0.02			
C_2H_6	0.32	0.31	0.09	0.01	
C_2H_5	0.09	0.10	0.08	0.06	
C_2H_4	0.55	0.44	0.26	0.10	

Table A2 : 3 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
BCH_4					
	2.4	2.57	0.88	0.05	
C_2H_3					
BCH_3					
	1.30	1.60	0.43	0.03	
C_2H_2					
BCH_2					
	0.01	0.01			
C_2H					
BC_2H					
	0.07	0.03			
C_2					
CH_4	0.06	0.06	0.06	0.03	
CH_3	0.40	0.40	0.10	0.07	0.13
CH_2	0.12	0.09	0.01		
CH					
	0.29	0.31	0.50		
BH_2					
BH					
	0.83	0.08	0.01		
C					
B	0.47	0.35			

*Corrected to monoisotopic

Table A2 : 4

Ion Abundances for Me_3Ga Source Temperature 30-50°

Ion*	70eV	50eV	20eV	12eV	10eV
$(Me_3Ga)_3$	0.08				
Me_3Ga_2	0.02				
C_3H_9Ga	1.07	1.36	1.42	8.22	0.65
C_3H_8Ga	0.08	0.08	0.07		
C_3H_6Ga	0.17	0.02	0.02		
C_2H_6Ga	71.37	74.54	91.06	91.58	96.42
C_2H_5Ga	0.95	0.87	0.43		
C_2H_4Ga	0.11	0.09			
C_2H_3Ga	0.05	0.05			
C_2H_2Ga	0.01	0.01			
CH_4Ga	0.94	0.69	0.17		
CH_3Ga	5.88	5.60	2.73	0.08	0.56
CH_2Ga	0.69	0.62	0.01		
CHGa	0.39	0.34			
CGa	0.21	0.12			
GaH_2	0.09	0.03			
GaH	0.13	0.09			
Ga	13.45	13.36	1.94	0.10	2.37
C_2H_6	0.01	0.01	0.01		
C_2H_5	0.05	0.05	0.01		

Table A2 : 4 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_4	0.27	0.37	0.04		
C_2H_3	0.17	0.12	0.01		
C_2H_2	0.15	0.07	0.01		
C_2H	0.06	0.01			
C_2	0.01	0.01			
CH_4	0.03	0.23	0.04		
CH_3	0.35	1.02	0.13		
CH_2	0.09	0.23	0.01	0.09	
CH	0.02	0.02	0.01		
C	0.01	0.01			

*Abundances corrected to monoisotopic.

Table A2 : 5

Ion Abundances for Me_3Ga Source Temperature 145-150°

Ion*	70eV	50eV	20eV	12eV	10eV
$(Me_3Ga)_3$					
Me_3Ga_2	0.02				
C_3H_9Ga	0.49	0.55	0.91	2.75	4.20
C_3H_8Ga	0.04		0.01		0.14
C_3H_6Ga	0.12	0.03	0.01		
C_2H_6Ga	72.30	74.37	97.0	96.81	95.22
C_2H_5Ga	0.78	0.89	0.49		
C_2H_4Ga	0.07	0.09			
C_2H_3Ga	0.04	0.04			
C_2H_2Ga	0.02	0.01			
CH_4Ga	0.93	0.73	0.19		
CH_3Ga	5.72	5.61	0.38	0.05	0.14
CH_2Ga	0.53	0.56	0.01		
CHGa	0.32	0.29	0.01		
CGa	0.13	0.09			
GaH_2	0.09	0.03	0.01		
GaH	0.09	0.08	0.01		
Ga	14.03	13.95	0.27	0.04	
C_2H_6	0.01	0.02	0.01		
C_2H_5	0.03	0.03	0.02		

Table A2 : 5 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_4	0.22	0.08	0.07		
C_2H_3	0.12	0.08	0.01		
C_2H_2	0.12	0.05	0.02		
C_2H	0.02	0.01			
C_2	0.01	0.01			
CH_4	0.14	0.09	0.08		
CH_3	0.68	0.46	0.39	0.34	0.23
CH_2	0.16	0.12	0.04		
CH	0.03	0.02	0.01		
C	0.01	0.05			

*Abundances corrected to monoisotopic.

Table A2 : 6

Ion Abundances for Me_3Ga Source Temperature 270°

Ion*	70eV	50eV	20eV	12eV	10eV
$(Me_3Ga)_3$					
Me_3Ga_2					
C_3H_9Ga	0.20	0.34	0.36	0.47	6.20
C_3H_8Ga	0.08	0.01	0.01	0.01	
C_3H_6Ga	0.05	0.02	0.01	0.01	
C_2H_6Ga	68.36	72.58	86.74	93.13	89.98
C_2H_5Ga	0.81	0.89	1.03	0.26	0.12
C_2H_4Ga	0.05	0.09	0.03	0.01	
C_2H_3Ga	0.12	0.05	0.02	0.01	0.01
C_2H_2Ga	0.06	0.01	0.01	0.01	0.01
CH_4Ga	0.75	0.70	0.49	0.13	0.06
CH_3Ga	6.40	6.30	5.50	2.95	1.89
CH_2Ga	0.42	0.56	0.14	0.01	0.01
CHGa	0.39	0.34	0.03	0.01	0.01
CGa	0.18	0.11	0.01	0.01	0.01
GaH_2	0.04	0.01	0.01		
GaH	0.14	0.09	0.01	0.01	0.02
Ga	15.1	15.3	3.82	1.93	1.15
C_2H_6	0.01	0.03	0.02	0.02	0.02
C_2H_5	0.02	0.05	0.05	0.03	0.02

Table A2 : 6 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_4	0.08	0.12	0.21	0.10	0.08
C_2H_3	0.08	0.13	0.06	0.01	0.01
C_2H_2	0.01	0.08	0.03	0.01	0.01
C_2H	0.02	0.01	0.01		
C_2	0.03	0.01			
CH_4	0.25	0.26	0.30	0.11	0.08
CH_3	1.06	1.00	0.93	0.45	0.28
CH_2	0.27	0.27	0.19	0.20	0.01
CH	0.05	0.04	0.01	0.01	
C	0.02	0.01	0.01		

*Abundances corrected to monoisotopic.

Table A2 : 7

Ion Abundances for Me_3In Source Temperature 30-50°

Ion*	70eV	50eV	20eV	12eV	10eV
C_3H_9In	0.17	0.16	0.25	0.24	0.31
C_3H_8In	0.01	0.01	0.01		
C_3H_6In	0.02	0.01			
C_2H_7In	1.41	1.25	1.59	1.43	1.77
C_2H_6In	61.92	61.08	77.41	81.13	87.67
C_2H_5In	1.57	1.41	0.89	0.70	0.59
C_2H_4In	0.20	0.14			
CH_4In	0.37	0.31	0.09	0.08	0.05
CH_3In	6.65	5.78	4.26	3.48	2.39
CH_2In	0.57	0.42	0.02	0.02	
CHIn	0.59	0.33			
CIn	0.26	0.18			
InH_2	0.06	0.01			
InH	0.08	0.06			
In	22.18	15.27	6.68	5.37	3.44
C_2H_6	0.09	1.00	0.96	0.54	0.36
C_2H_5	0.10	0.80	0.56	0.33	0.19
C_2H_4	0.51	2.11	2.29	1.30	0.82
C_2H_3	0.91	1.00	0.22	0.07	0.04
C_2H_2	0.27	0.60	0.13	0.09	0.11

Table A2 : 7 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H	0.03	0.06			
C_2	0.01	0.01			
CH_4	0.63	1.10	0.64	0.11	0.22
CH_3	0.71	5.83	3.95	3.33	2.36
CH_2	0.71	1.50	0.33	0.01	0.04
CH	0.09	0.19	0.03		
C	0.03	0.04			

*Abundances corrected to monoisotopic.

Table A2 : 8

Ion Abundances for Me_3In Source Temperature 150-175°

Ion*	70eV	50eV	20eV	12eV	10eV
C_3H_9In	0.076	0.07	0.08	0.14	0.13
C_3H_8In	0.01	0.01			
C_3H_6In	0.01	0.01			
C_2H_7In	1.33	1.22	1.38	1.69	1.89
C_2H_6In	50.47	57.10	64.46	82.14	86.16
C_2H_5In	1.01	0.96	1.12	0.46	0.27
C_2H_4In	0.42	0.19	0.43		
CH_4In	0.36	0.38	0.29	0.13	0.09
CH_3In	5.92	6.20	6.08	4.36	2.80
CH_2In	0.51	0.40	0.11	0.01	
CHIn	0.40	0.44			
CIn	0.25	0.24			
InH_2	0.02	0.01			
InH	0.08	0.07	0.02		
In	21.94	21.83	13.24	6.42	4.06
C_2H_6	0.68	0.57	0.60	0.39	0.32
C_2H_5	1.11	0.45	0.58	0.21	0.15
C_2H_4	2.13	1.80	2.13	0.92	0.80
C_2H_3	1.37	0.63	0.49	0.05	0.04
C_2H_2	0.55	0.34	0.21	0.07	0.08

Table A2 : 8 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H	0.07	0.04			
C_2	0.01	0.01			
CH_4	1.19	0.85	0.76	0.44	0.24
CH_3	6.14	4.45	4.60	2.28	2.24
CH_2	3.42	1.48	0.98	0.11	0.04
CH	0.40	0.21	0.09	0.01	
C	0.07	0.05	0.01		

* Abundances corrected to monoisotopic.

Table A2 : 9

Ion Abundance for Me_3In Source Temperature 270-300°

Ion*	70eV	50eV	20eV	12eV	10eV
C_3H_9In	0.03	0.03	0.03	0.07	0.09
C_3H_8In	0.01	0.01			
C_3H_6In	0.01	0.01			
C_2H_7In	1.11	1.03	1.15	1.52	2.00
C_2H_6In	49.20	46.1	58.3	72.64	84.44
C_2H_5In	0.86	0.82	0.91	0.37	0.18
C_2H_4In	0.82	0.65			
CH_4In	0.37	0.31	0.22	0.07	
CH_3In	6.24	6.18	5.21	3.05	3.01
CH_2In	0.43	0.43	0.23		
CHIn	0.38	0.31	0.07		
CIn	0.27	0.19	0.08		
H_2In	0.01	0.02			
HIn	0.08	0.07	0.02		
In	23.34	19.99	12.63	6.49	4.67
C_2H_6	0.59	1.31	1.34	1.16	0.96
C_2H_5	0.88	1.15	1.02	0.62	0.38
C_2H_4	2.08	3.94	4.20	2.85	1.93
C_2H_3	1.32	1.48	0.86	1.19	0.06

Table A2 : 9 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_2	0.59	0.90	0.37	0.12	0.06
C_2H	0.07	0.01			
C_2	0.01	0.01			
CH_4	1.17	2.13	1.96	0.78	0.31
CH_3	2.66	9.54	8.67	5.70	2.80
CH_2	2.77	3.10	2.23	0.26	
CH	0.40	0.51	0.21	0.03	
C	0.08	0.02	0.02		

*Abundances corrected to monoisotopic.

Table A2 : 10

Ion Abundances for Me_3Tl Source Temperature 30-40°

Ion*	70eV	50eV	20eV	12eV	10eV
C_3H_9Tl	0.04	0.03	0.08	0.11	0.30
C_3H_8Tl	0.01	0.01	0.02		
C_3H_6Tl	0.01				
C_2H_7Tl	1.06	0.55	1.36	2.30	2.27
C_2H_6Tl	45.7	42.9	77.49	95.70	95.60
C_2H_5Tl	1.41	1.04	0.87		
C_2H_4Tl	0.07	0.01			
CH_4Tl	0.26	0.21	0.09		
CH_3Tl	10.14	8.5	6.26	0.49	0.45
CH_2Tl	0.44	0.31	0.05		
CHTl	0.56	0.38			
CTl	0.33	0.19			
TlH_3	0.01	0.01			
TlH_2	0.01	0.01			
TlH	0.06	0.05			
Tl	34.75	42.9	12.20	1.40	1.36
C_2H_6	0.10	0.09	0.11		
C_2H_5	0.12	0.09	0.06		
C_2H_4	0.49	0.35	0.32		
C_2H_3	0.19	0.13	0.03		

Table A2 : 10 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_2	0.31	0.11	0.05		
C_2H	0.04	0.01			
C_2	0.01				
CH_4	0.55	0.25	0.16		
CH_3	2.85	1.82	0.80		
CH_2	0.17	0.11	0.01		
CH	0.05	0.03			
C	0.03	0.01			

*Abundances corrected to monoisotopic.

Table A2 : 11

Ion Abundances for Me_3Tl Source Temperature 140-160°

Ion*	70eV	50eV	20eV	12eV	10eV
C_3H_9Tl	0.04	0.03	0.05		
C_3H_8Tl					
C_3H_6Tl					
C_2H_7Tl	0.95	0.88	1.54	2.23	3.11
C_2H_6Tl	39.41	43.94	73.56	95.42	95.55
C_2H_5Tl	1.35	1.00	0.62		
C_2H_4Tl	0.07	0.01			
CH_4Tl	0.27	0.30	0.10		
CH_3Tl	10.40	8.78	6.39	0.49	
CH_2Tl	0.42	0.30			
CHTl	0.59	0.40			
CTl	0.37	0.21			
H_3Tl					
H_2Tl					
HTl	0.08	0.05			
Tl	37.93	28.46	13.75	1.16	1.33
C_2H_6	0.26	0.24	0.21		
C_2H_5	0.26	0.20	0.13		
C_2H_4	1.01	0.79	0.50		
C_2H_3	0.33	0.26	0.05		

Table A2 : 11 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_2	0.32	0.24	0.06		
C_2H	0.05	0.03			
C_2	0.02				
CH_4	0.61	0.44	0.23		
CH_3	3.06	4.12	2.17	0.68	
CH_2	0.40	0.62	0.11		
CH	0.08	0.14			
C	0.03	0.03			

*Abundances corrected to monoisotopic.

Table A2 : 12

Ion Abundances for Me_3Tl Source Temperature 270°

Ion*	70eV	50eV	20eV	12eV	10eV
C_3H_9Tl	0.03	0.08	0.17	0.25	
C_3H_8Tl					
C_3H_6Tl					
C_2H_7Tl	0.90	0.94	1.42	1.93	2.19
C_2H_6Tl	36.77	38.21	59.99	89.91	93.20
C_2H_5Tl	1.21	1.27	1.16		
C_2H_4Tl	0.08				
CH_4Tl	0.24	0.26	0.15		
CH_3Tl	9.75	10.23	8.08	1.28	0.54
CH_2Tl	0.44	0.37	0.11		
CHTl	0.54	0.49			
CTl	0.32	0.29			
TlH_3					
TlH_2					
TlH	0.07	0.07			
Tl	35.25	36.19	22.31	5.33	13.50
C_2H_6	0.28	0.29	0.31		
C_2H_5	0.33	0.40	0.23		
C_2H_4	1.13	1.29	1.00		
C_2H_3	0.48	0.56	0.15		

Table A2 : 12 (contd.)

Ion*	70eV	50eV	20eV	12eV	10eV
C_2H_2	0.35	0.37	0.12		
C_2H	0.05	0.05			
C_2	0.01	0.01			
CH_4	1.084	1.44	0.76		
CH_3	5.28	6.34	3.23	1.28	0.55
CH_2	0.95	0.11	0.38		
CH	0.18	0.21	0.03		
C	0.06	0.06			

*Abundances corrected to monoisotopic.

Appendix 3

Accurate masses found in the mass spectra of trivinylgallium.

Variation of ion abundances with source temperatures 30^{o}-270^{p}. Sample temperature -10^{o} to -5^{o}.

Table A3 : 1

Accurate Masses of Metal-Containing Ions in the Mass Spectrum of Trivinylgallium

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
152	$^{71}GaC_6H_9$	151.996570	151.996831	2
151	$^{71}GaC_6H_8$	150.988590		
150	$^{69}GaC_6H_9$	149.997412		
149	$^{69}GaC_6H_8$	148.989442	148.989002	3
140	$^{71}GaC_5H_9$	139.996570		
139	$^{71}GaC_5H_8$	138.988590	138.988679	1
138	$^{69}GaC_5H_9$	137.997412	137.996807	4
137	$^{69}GaC_5H_8$	136.989442	136.98882	4
136	$^{71}GaC_5H_5$	135.964469		
134	$^{69}GaC_5H_5$	133.965532	133.964873	5
128	$^{71}GaC_4H_9$*	127.996570	127.996042	2
127	$^{71}GaC_4H_8$*	126.988590	126.987513	8
126	$^{71}Ga^{12}C_3{}^{13}CH_6$	125.976010	125.975907	1
	$^{69}GaC_4H_9$	125.997412		
125	$^{71}GaC_4H_6$	124.972660	124.972394	1
	$^{69}GaC_4H_8$	124.989442		
124	$^{71}GaC_4H_5$	123.964690		
	$^{69}Ga^{13}C^{12}C_3H_6$	123.976852	123.976747	1
123	$^{71}GaC_4H_4$	122.956720	122.956363	2
	$^{69}GaC_4H_6$	122.973502	122.973120	2

Table A3 : 1 (contd.)

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
122	$^{69}GaC_4H_5$	121.965532	121.965218	2
121	$^{71}GaC_4H_2$	120.940780	120.940365	2
	$^{69}GaC_4H_4$	120.957562	120.957212	2
119	$^{69}GaC_4H_2$	118.941560	118.941201	2
113	$^{71}GaC_3H_6$	112.972660	112.971581	8
112	$^{71}GaC_3H_5$	111.964690	111.964108	4
111	$^{71}GaC_3H_4$	110.956720	110.956434	2
	$^{69}GaC_3H_6$	110.973502	110.973598	1
110	$^{69}GaC_3H_5$	109.965532	109.965718	2
109	$^{69}GaC_3H_4$	108.957562	108.957802	1
99	$^{71}GaC_2H_4$	98.956720		
	$^{71}Ga^{12}C^{13}CH_3$	98.952100	98.952150	1
98	$^{71}GaC_2H_3$	97.948750	97.948797	1
97	$^{71}GaC_2H_2$	96.940780	96.940720	1
	$^{69}Ga^{12}C^{13}CH_3$	96.952924	96.952971	1
	$^{69}GaC_2H_4$	96.957562	96.957501	1
96	$^{71}GaC_2H$	95.932810		
	$^{69}GaC_2H_3$	95.949592	95.949552	1
95	$^{69}GaC_2H_2$	94.941622	94.941692	1
94	$^{69}GaC_2H$	93.933652	93.933601	1

Table A3 : 1 (contd.)

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
93	$^{69}GaC_2$	92.925682	92.925399	2
87	$^{71}GaCH_4$	86.956720	86.956700	
86	$^{71}GaCH_3$	85.948750	85.954427	
85	$^{71}GaCH_2$	84.940780	84.940522	
	$^{69}GaCH_4$	84.957562	84.957223	
84	$^{71}GaCH$	83.932810	83.932744	
	$^{69}GaCH_3$	83.949592	83.949310	
83	^{71}GaC	82.924840	82.924601	2
	$^{69}GaCH_2$	82.941201	82.941298	1
82	$^{69}GaCH$	81.933652	81.933748	1
73	$^{71}GaH_2$	72.940839	72.940908	1
72	^{71}GaH	71.932819	71.932858	1
71	^{71}Ga	70.924840	70.924523	2
	$^{69}GaH_2$	70.941560	70.941564	1
70	^{69}GaH	69.933590	69.933544	1
69	^{69}Ga	68.925682		
56	C_4H_8	56.063760	56.063660	2
55	C_4H_7	55.055790	55.055676	2
54	C_4H_6	54.047820	54.047740	2
53	C_4H_5	53.039850	53.039855	1
52	C_4H_4	52.031880	52.031669	3

Table A3 : 1

Nom. mass	Ion	Mass calc.	Mass obs.	Error (P.P.M.)
51	C_4H_3	51.023910	51.023734	4
50	C_4H_2	50.015940	50.015798	3

Table A3 : 2

Ion Abundances for $(CH_2{=}CH)_3Ga$

	Source Temp. 150°			Source Temp. 30-50°		
Ion	70eV	20eV	10eV	70eV	20eV	10eV
C_6H_9Ga	.03	.04	.09	.05	.05	.07
C_6H_8Ga	.03	.04	.09	.01	.02	.07
C_5H_9Ga	.01	.02	.05	.01	.02	.04
C_5H_8Ga	.04	.02	.05	.02	.02	.04
C_5H_8Ga	.04	.01	.25	.07	.05	.04
C_4H_9Ga	.05	.05	.09	.04	.05	.08
C_4H_8Ga	.14	.13	.16	.11	.14	.10
C_4H_6Ga	40.52	42.50	56.91	37.60	44.57	53.05
C_4H_5Ga	.04	.07	.06	.11		
C_4H_4Ga	.08	.07	.13	.06	.16	.26
C_4H_2Ga	.09	.09	.13	.08	.12	.11
C_3H_6Ga	.40	.40	.36	.18	.38	.27
C_3H_5Ga	.02	.05	.05	.02	.07	.01
C_3H_4Ga	.09	.14	.13	.06	.07	.13
C_2H_4Ga	9.17	11.00	3.46	8.82	9.97	3.24
C_2H_3Ga	13.94	14.46	18.63	15.21	17.07	24.62
C_2H_2Ga	.28	.53		.57	.03	
C_2HGa	.24	.26	.23	.18	.36	.09
C_2Ga	.45	.53	.56	.40	.63	.62

Table A3 : 2 (contd.)

	Source Temp. 150°			Source Temp. 30-50°		
Ion	70eV	20eV	10eV	70eV	20eV	10eV
CH_4Ga	.41	.49	.28	.33	.41	.09
CH_3Ga	.12	.13	.16	.10	.11	.05
CH_2Ga				.07	.01	
CHGa	.20	.23	.33	.16	.24	.31
CGa	.45	.51	.43	.04	.35	.49
H_2Ga	.31	.71	.30	.80	.27	.40
HGa	.09	.07	1.10	.06	.03	.60
Ga	21.19	16.34	9.95	23.84	17.05	11.25
C_4H_x	3.00	3.00	2.63	2.26	2.45	1.93
C_3H_x	3.21	3.09	1.27	2.86	2.57	.87
C_2H_x	5.16	4.70	2.06	5.65	2.66	1.07
CH_x	.11	.05		.17	.04	

Table A3 : 2 (contd.)

Source Temp. 250°

Ion	70eV	20eV	10eV
C_6H_9Ga	.01	.08	.20
C_6H_8Ga	.02	.13	.20
C_5H_9Ga	.03	.03	.07
C_5H_8Ga	.05	.06	.07
C_5H_5Ga	.05	.11	.13
C_4H_9Ga	.16	.11	.13
C_4H_8Ga	.22	.20	.20
C_4H_6Ga	37.37	41.88	54.40
C_4H_5Ga	.05	.01	
C_4H_4Ga	.05	.06	.18
C_4H_2Ga	.16	.80	.18
C_3H_6Ga	.81	.93	.82
C_3H_5Ga	.16	.09	.14
C_2H_4Ga	7.87	10.19	4.14
C_2H_3Ga	10.72	12.25	15.57
C_2H_2Ga	.29	.20	.36
C_2HGa	.26	.65	.68
C_2Ga	.53	.39	.68
CH_4Ga	.48	.53	.20
CH_3Ga	.32	.16	.27

Table A3 :2 (contd.)

Source Temp. 250°

Ion	70eV	20eV	10eV
CH_2Ga			
CHGa	.32	.06	.41
CGa	.53	.07	.59
H_2Ga	.81	.58	.68
HGa	.53	.10	.14
Ga	19.23	14.24	8.76
C_4H_y	4.84	4.69	4.24
C_3H_z	4.80	4.64	1.92
C_2H_m	8.78	6.86	4.60
CH_n	.33	.27	.07

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